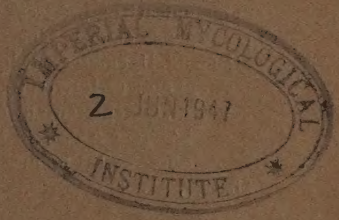
COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1943



VOLUME XL

№ 6

ÉDITION DE L'ACADÉMIE DES SCIENCES DE L'URSS
MOSCOU

AVIS AUX AUTEURS

Les «Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS» paraissent tous les dix jours. Neuf numéros composent un volume pourvu d'une table des matières. Il y a quatre volumes par année.

Les «Comptes Rendus de l'Académie des Sciences de l'URSS» en de courtes communications précisent l'essentiel des travaux en préparation. Ces articles, ne dépassant pas en règle générale quatre pages, sont donnés en anglais, en français ou en allemand. Ils embrassent les sciences mathématiques, physiques, naturelles et appliquées, mettant au jour les résultats de recherches scientifiques en cours ou qui viennent d'être achevées, et représentant ainsi les plus récentes données de l'investigation scientifique.

L'auteur a droit à 50 exemplaires de son article.

Adressez les manuscrits à la Rédaction des «Comptes Rendus», Moscou, Wolkhonka, 14.

30 Août

COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

COMITÉ DE RÉDACTION

A. Arbusov, de l'Académie, A. Borissiak, de l'Académie, V. Chlopin, de l'Académie, A. Deborin, de l'Académie, A. Fersman, de l'Académie, A. Frumkin, de l'Académie, A. Kolmogoroff, de l'Académie (vice rédacteur), L. Orbeli, de l'Académie (rédacteur en chef), A. Richter, de l'Académie, S. Soboleff, de l'Académie, S. Wawilow, de l'Académie (vice rédacteur)

NOUVELLE SÉRIE

11-me année

Paraissant tous les dix jours

1943

VOLUME XL, № 6

TABLE DES MATIÈRES

MATHÉMATIQUES Page

L. Lusternik. On the Number of Solutions of a Variational Problem 215

PHYSIQUE

M. A. Markov. Electrodynamics of Dirac-Fock-Podolsky and the Self-Energy of the Electron 218

PHYSIQUE APPLIQUÉE

V. V. Zelinsky. Fluorescent Screens of High Resolving Power 220

PHYSIQUE DU GLOBE

V. L. Ginsburg and **N. N. Soboleff.** On Secondary Light Scattering in the Atmosphere and on Polarization Anomalies during Twilight 223

CHIMIE

A. A. Balandin and **M. N. Marushkin.** Formation of Olefins from Higher Paraffinic Hydrocarbons 226

D. I. Riabchikov. Products of the Reaction of Thiosulphatoplatinites with Certain Amines 229

CHIMIE PHYSIQUE

G. B. Boky and **E. E. Wainstein.** On the Crystal Chemistry of the Laves Phases 232

N. N. Sirota. Kinetics of Isothermal Coagulation of not Colliding Particles . 234

GÉOLOGIE

B. P. Krotov. Geological Evidence Favouring the Search for Iron-Nickel Ores of the Anatol Type in the Middle Urals 239

V. I. Yavorsky. Kuznetsk Series at the Eastern Limb of the Kemerovo Syncline 242

PHYSIOLOGIE DES PLANTES

A. A. Nichiporovich. On the Integrity of Latex Vessel System in Kok-Saghyz and Krym-Saghyz 245

ENTOMOLOGIE

A. S. Kosmachevsky. *Melolontha* Larvae as Affected by Soil Humidity . . . 248

PHARMACOLOGIE

V. V. Reverdatto. New Cardiaca Yielding Plants from the Family *Cruciferae* 251

Édition de l'Académie des Sciences de l'URSS
Moscou 1943

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

MATHEMATICS

ON THE NUMBER OF SOLUTIONS OF A VARIATIONAL PROBLEM

By L. LUSTERNIK

(Communicated by S. Soboleff, Member of the Academy, 6. IV. 1943)

We shall extend to the case of variational problems the results obtained in our previous paper (1) concerning the functions of a finite number of variables.

Let R be a compactum (the following can also be extended to bicompact spaces).

Consider a class of closed sets in R that we call K-sets. We suppose that every closed subset of a K-set is a K-set itself. Let, for instance, $R(S_2, a, b)$ be the compact space considered in (2-4) consisting of rectifiable curves on S_2 with fixed end-points a and b. We call K-set in $R(S_2, a, b)$ every closed family M of curves q, for which the length of q' is a continuous functional on M.

By K-deformation of a K-set M in R we mean the deformation that carries M into a K-set. The Δ-cycle z on R will be called K-cycle if z considered as a subset of R is a K-set. The class (z) of K-cycles on R will be called K-class, if it consists of K-cycles and, together with any of its cycles z, it contains all K-cycles z', Δ-homologous to z or to some multiple of z (i. e. homologous to pz, where $p > 0$, or, if we deal with homologies modulo q, $p < q$).

Consider a functional J on R and the «surfaces» determined by the equations $J = c$.

A closed set A on a surface $J = c$ will be called K-critical, if, whenever $\varepsilon > 0$ is sufficiently small, it is possible to choose such $\alpha > 0$ that every K-set M, lying in the domain $J < c + \alpha$ at the distance greater than or equal to ε from A, can be transformed by a K-deformation into a set M' belonging to the domain $J < c - \alpha_1 < c$.

Example. Let $J(q)$ be the length of the curve q in $R(S_2, a, b)$. Then the totality of all curves of the given length c is a K-critical set in $R(S_2, a, b)$.

Let (z) be a K-class of n-dimensional Δ-cycles in R. Denote by c the greatest lower bound of the maxima of J on the cycles z from (z). The surface $J = c$ cannot contain void K-critical sets, because otherwise the K-cycles z' of the class (z) belonging to $J < c + \alpha$ could be transformed into the cycles of the same class belonging to $J < c - \alpha_1 < c$, when $\alpha > 0$ is sufficiently small, and thus the g. l. b. of the maxima of J on (z) could not exceed $c - \alpha_1 < c$, that is impossible.

Example. Denote by (T_n) the totality of n-dimensional Δ-cycles on $R(S_2, a, b)$ homologous to T_n and constituting the K-sets in the above sense [T_n are defined in (2)].

Let c_n be the g. l. b. of maxima of lengths of the curves belonging to the families contained in (T_n). There exist then a geodesic of the length c_n. We thus obtain the sequence of geodesics on S_2 of lengths c_n joining the points a and b, the existence of which was first established by Morse (3).

Let (x) and (z) be some $\mathfrak{R}$-classes of Δ-cycles of $(n+m)$ and n dimensions, respectively, and (Y) — a class of mutually homologous m-dimensional ∇-cycles. We say that the K-class (z) is subjected to the class (x) by means of the class (Y), if for every x from (x) the intersection $Y \times x$ belongs to (z).

Remark. The intersection of an upper cycle with a lower one was defined by Čech for the case of complexes, and the definition can be extended to an arbitrary compactum. It is essential for us that the intersection $Y \times x$, where Y is an m-dimensional Δ-cycle and x is an $(n+m)$-dimensional Δ-cycle, is an n-dimensional Δ-cycle contained in the set-theoretical intersection of x and Y, i. e. in the set-theoretical intersection of x with the «carrier» of the upper cycle Y [under the carrier of a ∇-cycle we understand the closed set $\overline{Y}$ such that: 1) Y can be determined by a sequence of functions vanishing outside every neighbourhood of $\overline{Y}$, 2) $\overline{Y}$ is irreducible with respect to the property 1].

Let (x) and (z) be some $\mathfrak{R}$-classes of $(n+m)$-dimensional and n-dimensional Δ-cycles.

Suppose that the class (z) is subjected to (x) by means of a ∇-class (Y) of m-dimensional cycles, and denote by c_1 and c_2 the g. l. b-s of the maxima of the functional J on the cycles belonging to (x) and (z), respectively. We evidently have: $c_1 \leqslant c_2$.

Theorem 1. *If $c_1 = c_2 = c$, then every $\mathfrak{R}$-critical set on the surface $J = c$ contains an m-dimensional Δ-cycle y dual to Y, i. e. such that $\varkappa(y, Y) \neq 0$.*

Let A be an abritrary K-critical set on $J = c$. If $\varkappa(y', Y) = 0$ for every m-dimensional Δ-cycle y' from A, then (according to Pontrjagin-Alexandroff's theorem) [4]) Y can be «drawn off» the set A, i. e. the Δ-homology class (Y) contains a cycle $Y' \sim Y$ lying outside A at a distance $\varepsilon > 0$ from A. Let $\alpha > 0$ be such a number that every K-set lying in the domain $J < c + \alpha$ at the distance less than or equal to ε can be carried into the domain $J < c - \alpha_1 < c$ by means of a K-deformation. The domain $J < c + \alpha$ contains a cycle x_1 from the class (x).

The intersection $Y_1 \times x_1$ determines an n-dimensional Δ-cycle z_1 of class (z) belonging to the set-theoretical intersection of Y_1 and x_1 and, consequently, lying in the domain $J < c + \alpha$ at the distance greater than or equal to ε from A.

According to the definition of α, z_1 can be transformed by means of a K-transformation into a cycle z_2 lying in $J < c - \alpha_1 < c$. Since $z_2 \sim z_1$, z_2 belongs to (z).

The maximum c' of J on z_2 does not exceed $c - \alpha_1$, and thus the g. l. b. of the maxima of J on the cycles belonging to the class (z) does not exceed $c - \alpha_1 < c = c_2$, contrary to our hypothesis.

This theorem is a generalization of a theorem proved in [1]) for the case of functions of finitely many variables.

Application to the Theory of Geodesics. Let $R^1 = R(S_2, a, b)$ be the space mentioned above that consists of rectifiable curves on the space S_2 of genus O joining the points a and b. Let further $J(q)$ denote the length of the arc $q \in R$ and R_N — the compact subset $J \leqslant N$ of the space R. T_n belongs to R_N, when N is sufficiently large. The K-class (T_n) determines the number c_n — the g. l. b. of the maxima of J on the sets of class (T_n). As we know, there exists a geodesic q_n of length c_n. The cited papers [1], [2]) contain the investigation of upper and lower homology groups and of the intersection ring in $R(S_2, a, b)$. It follows from these results that

$$Y^m \times T_{m+n} \sim c_{m,n} T_n$$

where Y^m are m-dimensional ∇-cycles defined in [2]). As to the coefficients $c_{m,n}$ [2]), $c_{1,n} = 0$, when n is odd, $c_{1,n} = 1$, when n is even, and $c_{2,n} \neq 0$. Consequently, $T_m \times Y'$ is homologous to zero or to T_{m+1}, according as m is odd or even. If m is even, the class T_m is subjected to the class T_{m+1} by means of Y'.

The Δ-cycle dual to Y' is T_1. Therefore, if $c_m = c_{m+1} = c$, then, m being even, the family of geodesics of length c joining the points a and b is homologous to qT_m, $q \geqslant 1$, which is possible only if all geodesics passing through a pass also through b, and the length of the arc between a and b of every geodesic has the length c.

The case $c_m = c_{m+2} = c$ must be excluded, because otherwise, T_m being subjected to T_{m+2} by means of Y^2, there would exist a two-parameter family of geodesics of length c joining the points a and b, which is impossible. Thus, we have proved

Theorem 2. *The lengths of geodesics $c_1 \leqslant c_2 \leqslant c_3 \leqslant \ldots$ joining any two points a and b on the surface of genus O satisfy the exact inequalities $c_m < c_{m+2}$ for every m. If $c_m = c_{m+1} = c$ for m even, then every geodesic passing through a passes through b, too, so that the length of the arc of the geodesic cut out by the points a and b is c.*

The latter case takes place, for instance, on the sphere, when a and b are diametrically opposits points.

V. A. Stekloff Mathematical Institute.
Academy of Sciences of the USSR.

Received
6. IV. 1943.

REFERENCES

[1] L. Lusternik, C. R. Acad. Sci. URSS, XXXVIII, No. 2–3 (1943). [2] L. Lusternik, ibid., XXXIX, No. 3 (1943). [3] Morse, The Calculus of Variations in the Large. [4] P. S. Alexandroff, Bull. Acad. Sci. URSS, sér. math., 6, No. 5 (1943).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

PHYSICS

ELECTRODYNAMICS OF DIRAC-FOCK-PODOLSKY AND THE SELF-ENERGY OF THE ELECTRON

By M. A. MARKOV

(Communicated by S. I. Wawilow, Member of the Academy, 19. V. 1943)

In an electrodynamics set forth in the form of D. F. P. (1) new difficulties arise in the way of an electromagnetic interpretation of the self-energy of the electron.

In fact, we have here a system of equations:

$$i\hbar \frac{\partial \Psi}{\partial t_s} = \left\{ c\vec{\alpha}_s \left(P_s - \frac{e_s}{c} \vec{A}_s \right) + \beta_s m_s c^2 + e_s \varphi_s \right\} \Psi \quad (s = 1, 2, 3, \ldots, n) \tag{1}$$

$$\frac{\partial^2 \varphi}{\partial X^2} + \frac{\partial^2 \varphi}{\partial Y^2} + \frac{\partial^2 \varphi}{\partial Z^2} - \frac{1}{c^2} \frac{\partial^2 \varphi}{\partial T^2} = 0; \quad \nabla^2 \vec{A} - \frac{1}{c} \frac{\partial^2 \vec{A}}{\partial T^2} = 0. \tag{2}$$

The equation of the particle motion (1) involves no field energy, i. e. does not contain the expression

$$\int \frac{E^2 + H^2}{8\pi} dV. \tag{3}$$

What is more, the expression (3) in point of principle cannot possibly be introduced into the equation of the particle motion (1) without disturbing the relativistic symmetry of the system of equations (1) and (2).

As the field and particles are described by different times, even the conservation laws are formulated in these times for the field and for the particles independently.

The circumstance that the electromagnetic field and the electron are considered as two interacting systems of which none can be reduced to the other, is most clearly expressed in Dirac's electrodynamics. Therefore all attempts in the frame of the electrodynamics of Maxwell-Lorenz-Dirac to reduce the inert mass of the electron to the electromagnetic mass are incompatible with the mathematical apparatus and the physical conceptions employed by this theory.

There are also difficulties in this theory connected with the fact that divergent expressions appear in many of its results. As has been pointed out above, they have no physical sense within the limits of this theory.

The «superfluous» character of these divergent expressions is emphasized by the fact that in computing all really observed effects in electrodynamics, the divergent expressions are simply ignored and the respective expression for the mass of the electron is written in the equation independently of the field.

From that point of view the only consistent problem in the frame of the given theory is an attempt to free it entirely from such expressions, instead of endeavouring to obtain them in a finite form. Along this line only one attempt has been reported in literature. It bears upon non-quantum electrodynamics(2).

Very likely the same problem can be solved by suitably changing the relation between the electron and the radiation [see note on non-linear interaction ([3])].

It might appear that the problem of interpretation of the inert mass of the electron as an electromagnetic mass has been considered in non-linear electrodynamics (Mie, Born and others). Unfortunately, we have here up to the present not a single consistent system of quantum equations of motion. At any rate in an attempt to write the equation of motion for the particle and field consistently in a relativistic manner, we should introduce for every particle and accordingly for the field their proper times, which signifies that here, too, the field and the particle would be considered as interacting systems, but at the same time as systems different in principle.

P. N. Lebedev Physical Institute.
Academy of Sciences of the USSR.

Received
19. V. 1943.

REFERENCES

[1] Sow. Phys., 2, 468 (1932). [2] P. A. M. Dirac, Proc. Roy. Soc., A, 167, 148, 138 (1938). [3] M. Markov, C. R. Acad. Sci. URSS, XL, No. 1 (1943).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

TECHNICAL PHYSICS

FLUORESCENT SCREENS OF HIGH RESOLVING POWER

By V. V. ZELINSKY

(Communicated by S. I. Wawilow, Member of the Academy, 27. IV. 1943)

To obtain visible image in the ultra-violet it is desirable to possess a bright fluorescent screen of high resolving power. Such screens are useful e. g. in ultra-violet spectroscopy. The material used for obtaining screens of high resolving power must be homogeneous and the fluorescence must be concentrated in a thin surface layer. For these purposes are suitable plastics, dyed on the surface with a fluorescent substance*.

Celluloid, acetylcellulose and methylpolymetacrylic plastic were used as a material. No marked difference between these materials could be observed. Further in this article we consider screens of methylpolymetacrylic plastic.

We tried for dying purposes over 250 substances. Bright screens were obtained with rhodamine 6G, 3-aminophthalimide, 4-aminophthalimide, 3-methylaminophthalimide, 4-methylaminophthalimide, 3, 6-diaminophthalimide and 3, 6-dimethylaminophthalimide.

The fluorescence brightness of the screens was measured by means of a Fabry-Gelhoff photometer and expressed in per cent to the brightness of the uranylpotassium sulphate screen; the quantum yield of this latter substance had been found by Gurevich and Chakhrov (') to be equal to 1.

Fluorescence was excited by a mercury lamp light, filtered through Wood's black glass (λ=366 mμ). Under all the variations of dye conditions, viz. time, temperature and concentration of dyestuff in solutions, the maximum brightness obtained with rhodamine and phthalimides was about 12—15%. An increase in coloration intensity beyond a certain optimum led to no increase in brightness, but rather to a certain decrease, because of concentrational quenching.

Attempts were made to dye screens with dyestuff mixtures. The brightness of screens dyed with a mixture of 3-amino and 3, 6-diaminophthalimides reached 22—24% of the uranylpotassium sulphate brightness. Substitution of 3-aminophthalimide for 4-amino, 3-methylamino or 4-methylaminophthalimides gave nearly the same results. Substitution of 3, 6-diaminophthalimide or rhodamine 6G gave a decrease of brightness.

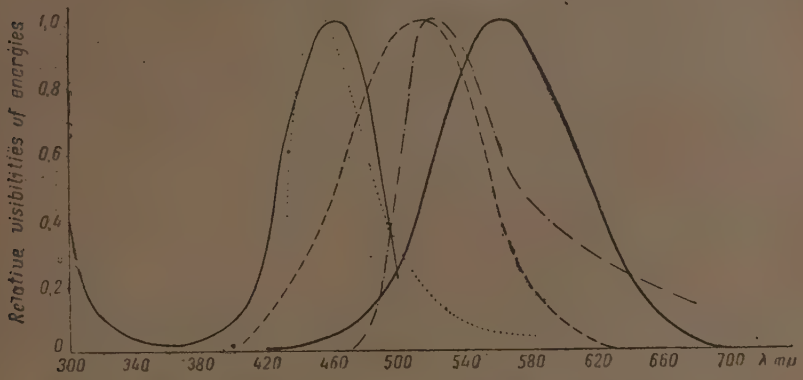
To obtain a screen with a brightness of about 24%, a thoroughly ground plate of methylpolymetacrylic plastic was placed in a mixture of 3 parts of alcohol and 2 parts of water, containing 0.4% of 3-aminophthalimide and 0.4% of 3, 6-diaminophthalimide, and was kept in this mixture about 30 minutes, the temperature being about 50°. The plate was then dried at room temperature and upon drying cleansed with cotton moistened with alcohol. From one of the faces of the plate the layer obtained was removed by grinding. The resolving power of the screens prepared was about 200—300 lines per millimeter.

---

* Screens of dyed plastics have been obtained some time ago in our laboratory by E. M. Brumberg and M. D. Gorodonov.

In order to find out the causes underlying the increase in the brightness of screens dyed with the above-mentioned mixture, and the possibility of increasing it farther, we determined the energy distribution in the fluorescence spectra of screens stained with 3-aminophthalimide, 3, 6-diaminophthalimide and of those stained with a mixture of these substances, as well as the energetical yield of fluorescence of a screen stained with this mixture. Distribution of energy in spectra was measured by means of a König-Martens' photometer. The results are given in the curves I, II, III of the figure.

The maximum of the curve representing energy distribution in the fluorescence spectrum of the screen dyed with 3-aminophthalimide (I) lies at about 450—460 mμ. The maximum of the curve that gives energy distribution in the fluorescence



I—curve of energy distribution in fluorescence spectrum of a screen stained with 3-aminophthalimide; II and III—curves of energy distribution in spectra of screens stained with 3, 6-diaminophthalimide and with mixture; IV—absorption curve for 3, 6-diaminophthalimide

spectrum of the screen dyed with 3, 6-diaminophthalimide lies at about 510—530 m μ (II). As to the curve of a screen dyed with the above-mentioned mixture (III), its shape does not differ from that of the preceding curve (II). This circumstance shows that the light emitted by 3-aminophthalimide molecules is absorbed totally by the molecules of 3, 6-diaminophthalimide.

This fact may be taken to mean that the maximum of an absorption spectrum of 3, 6-diaminophthalimide (curve IV) which lies at about 450—470 mμ, coincides with that of curve I representing the fluorescence spectrum of the screen dyed with 3-aminophthalimide.

As the minimum of 3, 6-diaminophthalimide absorption spectrum lies at 350—370 mμ, the absorption of the exciting light (366 mμ) by the screen stained with that substance will be small.

Now, if we take into account that a 3-aminophthalimide stained screen totally absorbing the wave-length 366 mμ is emitting in the region of feeble sensitivity of the eye, it will be clear that a sreen stained with a mixture is brighter than the former. Indeed, molecules of 3-aminophthalimide totally absorb the exciting light, but they emit light which acts but feebly upon the human eye; when in mixture, the light emitted by 3-aminophthalimide is totally reabsorbed by 3, 6-diaminophthalimide molecules, the emission of the latter lying between the maxima of eye sensitivity curves for day (curve V) and twilight (curve VI) vision.

The energy yield of the screen coloured with a mixture of 3- and 3,5-aminophhalimides under optimal conditions has been measured by comparing its brightness to that of fluorescein in alcohol solution. The colour of the alcohol solution of fluorescein and that of the screen proved to be nearly coincident. The energy

yield of fluorescein has been measured by S. I. Wawilow ([2]). The yield of the screen fluorescence was found to be 0.45—0.5 (exciting light 366 mμ).

As may be seen from elementary calculation, the wave-length of exciting light being 366 mμ and the maximum of fluorescence spectrum about 520 mμ, the energy yield cannot exceed 0.67. Taking into consideration the steep fall of the fluorescence curve towards the short waves and sloping run in the long-wave direction, the yield has to be still less. Thus, the yield of a phthalimide mixture stained screen does not differ much from the theoretically possible one.

The fact that the brightness of our screens is considerably smaller than that of uranylpotassium sulphate is accounted for by the fact that in the case of a thin plate with parallel ground faces only that part of the light emitted in all directions can issue through the front surface, which falls on the facet at an angle smaller than that of the total inner reflection. The major part of light would issue through the side surfaces and closely near them, and would not hit the eye. If the plate is a granular structure, as in the case of uranylpotassium sulphate, then as a result of innumerable reflections and scatterings some additional amount of light will issue through the front facet. This will naturally reduce the resolving power. Indeed, a screen prepared from grains of the same plastic, stained under the same conditions as the plate, was found to possess a brightness of about 90—95% of that of the uranylpotassium sulphate screen.

State Optical Institute,

Received
27. IV. 1943.

REFERENCES

[1] M. M. Gurevich and L. J. Chakhrov, Bull. Acad. Sci. URSS, sér. phys., No.3, 509 (1938). [2] S. I. Wawilow, ZS. f. Phys., 22, 266 (1924).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

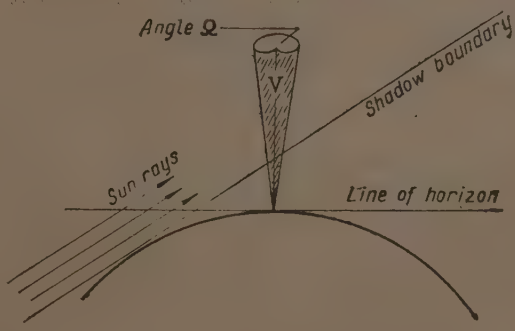
GEOPHYSICS

ON SECONDARY LIGHT SCATTERING IN THE ATMOSPHERE AND ON POLARIZATION ANOMALIES DURING TWILIGHT

By V. L. GINSBURG and N. N. SOBOLEFF

(Communicated by S. I. Wawilow, Member of the Academy, 15. IV. 1943)

From an analysis of the question as to the polarization of crepuscular light (1) one is led to conclude that these anomalies are associated in the first line with secondary light scattering in the atmosphere (2). In order to obtain quantitative evidence, we have to extend to the case of twilight the theory of polarization of sky luminosity, which has been developed for positive Sun altitudes only (2). In the case of twilight, however, we are faced with a number of peculiarities that make the problem an exceedingly difficult one*, preventing one to obtain conclusive semi-quantitative formulae, which are obtainable with $h \geqslant 0°$ (3). Nevertheless, a mere qualitative analysis of the problem gives us insight into the main experimental results (1, 2); the presence of the first deep minimum on the polarization curve, as well as other peculiarities of scattering at twilight point to an increased rôle of secondary scattering.



Let us assume for simplicity sake that observation is carried out at the zenith, the observer's eye being hit by the light from volume V, bounded by solid angle Ω (see figure).

In the case of positive Sun altitude the primary scattering we are interested in takes place all over V. The secondary scattering also proceeds all over this volume, but the source of the radiation field generating this secondary scattering is the whole atmosphere. During twilight primary scattering takes place only in that part of V which is above the boundary of the shadow, while the whole of the V participate in the secondary scattering; the secondary scattering is due to the radiation emitted by the volume which is directly illuminated by the Sun (see figure)**. Up to altitudes of the order of 100 km the

* For instance, let us point to the asymmetry of twilight illumination, and to the necessity to allow in that case for the Earth's curvature and light absorption in the atmosphere.

** The plane of the figure coincides with that of the vertical. It is essential that the boundary of the shadow is not a plane, owing to which the secondary scattering in the lower portion of volume V is due also to the radiation emitted in a direction perpendicular to the plane of the drawing.

density of the atmosphere makes a rapid drop; the decrease goes on mainly exponentially.

The intensity of the primary scattering is proportional to density; hence, it drops rapidly, too, according as the depression of the Sun increases.

Unlike this, secondary scattering decreases at first rather slowly, its reduction being accounted for by a decrease in the volume of the illuminated portion of the atmosphere and by absorption. When the Sun stands at the horizon, the intensity of secondary scattering makes up about 19 per cent of the intensity of primary scattering ([3]).

It follows from what has been said above that during twilight secondary scattering may already be as large as the primary one. As a matter for regret, no reliable calculation of the corresponding relation between the intensities seems to be possible. Further on, according as the Sun sinks behind the horizon, the regions of the atmosphere which are illuminated by the Sun are more and more removed from the lower part of the volume of V which plays the basic part in secondary scattering. Therefore the rôle played by absorption which strongly depends on distance, begins to play a gradually increasing part, while the intensity of secondary scattering decreases. At the same time, beginning with heights of about 100 km, the decrease in the density of the atmosphere and, consequently, in the intensity of primary scattering, proceeds at a slower rate.

It follows from what has been said above that as soon as the Sun sinks behind the horizon; polarization of the sky light must decrease rapidly, while the respective distances of the neutral points from the Sun and the antisolar point must grow, which is experimentally observed. It is quite natural, with this, that polarization decreases monotonously, in so far as it is the resultant polarization of primarily and secondarily scattered light that is concerned.

The high intensity of secondary scattering during twilight must also tell upon the measurement of atmosphere density by means of photometrical treatment of crepuscular light ([4]).

The results of investigations in which no allowance for secondary scattering is being made ([4]), may be essentially affected by this neglect.

In addition to what has been said in an earlier note ([2]), let us dwell here on the relation between polarization anomalies and the electrical properties of the ionosphere.

For altitudes smaller than 150 km, polarization anomalies can certainly not be associated with ionic layers ([2]). However, a correlation with the critical frequency is particularly conspicuous for layer E ([1]). Hence it follows univocally that the relation between the two phenomena is no direct, but rather an indirect one.

This relation is most probably determined by some dynamical processes in the atmosphere, whose effect was both upon the concentration of ions in the layer E and upon the distribution and movement of air masses, on which primary and secondary scattering takes place. For altitudes of about 200 km and above polarization may be affected by the variation of atmosphere composition (ions, electrons, etc.) directly. However, in this case, too; the influence can be but a secondary one. This is evidenced both by the presence of anomalies at smaller heights, where we are sure not to deal with any change in the composition; and by a number of other considerations, as well. At considerable altitudes ([5]) polarization becomes so insignificant that it cannot possibly be taken to account for such a degree of polarization whatever the change in composition. Along with a decrease in polarization; there takes place also rotation of the polarization plane ([5]).

If we were to assume; which is quite natural, that we have in this case to deal with a rotation of the plane of polarization of scattered light, this effect would point to an asymmetrical illumination in the scattering volume of the atmosphere.

An asymmetry of this kind might take place, if e. g. the solar rays would bend, or if the scattering layer would receive more light on the one side from the

plane of the vertical than on the other, etc. In the case of an illumination symmetrical with respect to the plane of the vertical, the existence of an ionic layer would at any rate not lead to the rotation of the polarization plane.

The problem as to the processes in the stratosphere that call forth polarization anomalies (non-monotonous polarization, rotation of the polarization plane) and act upon the concentration of ions above the spot of observation is, certainly, of great interest.

P. N. Lebedev Physical Institute,
Academy of Sciences of the USSR.

Received
16. IV. 1943.

REFERENCES

[1] V. M. Bovsheverov, I. A. Khvostikov and others, C. R. Acad. Sci. URSS, XXVI, 897 (1940); Bull. Acad. Sci. URSS, sér. géophys., 657 (1940). [2] V. L. Ginsburg, C. R. Acad. Sci. URSS, XXXVIII, No. 9 (1943). [3] J. J. Tichanowsky, Phys. ZS., 28, 680 (1927). [4] В. Е. Фесенков, Астр. журн., 7, вып. 2 (1930); Н. М. Штаудe, Фотометрич. наблюдения сумерек, 1936. [5] G. V. Rosenberg, C. R. Acad. Sci. URSS, XXXVI, 288 (1942); Z. L. Ponizovsky and G. V. Rosenberg, ibid., XXXVII, 249 (1942).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

CHEMISTRY

FORMATION OF OLEFINS FROM HIGHER PARAFFINIC HYDROCARBONS

By A. A. BALANDIN and M. N. MARUSHKIN

(Communicated by V. G. Chlopin, Member of the Academy, 10. V. 1943)

It has been shown as far back as by Thorpe and Young (1) that solid paraffin is decomposed by pyrolysis into smaller molecules of paraffinic and olefinic hydrocarbons. It seemed of interest whether the yield of olefins could be increased by the use of an active and specific chromium catalyst; used by us for the dehydrogenation of butane (2). No data are available in literature as to catalytic dehydrogenation of paraffins above C_{10}, except for one; scarcely reliable patent communication (3).

The initial paraffin was hard, white, m. p. 50°. By its properties it belonged to the type B No. 142 of the 3960 All-Union Standard on petroleum paraffins (4).

Molecular weight determination: 0.0194 g of substance; 0.0952 g of camphor, $\Delta t = 14.1°$; 0.0125 g of substance; 0.0787 g of camphor, $\Delta t = 11.1°$. Found: $M = 557$; 551. Average 554.

This corresponds to an average number of carbon atoms about C_{40}. It is well known that solid paraffin is a complex mixture of saturated hydrocarbons [thus Kraft (5) was able to isolate compounds from $C_{17}H_{36}$ to $C_{36}H_{74}$, this forming only half of the total number].

Experiments were carried out in a quartz tube ($d = 12$ mm) with a catalyst (layer 35 cm, weight 8.2 g, volume 23 cm^3). The tube was placed in an electric furnace with a thermoregulator. The thermocouple was imbedded in the layer. Melted paraffin was added from a heated dropping funnel. Solid and liquid reaction products were collected in a receiver with a reflux condenser, and gaseous products could be either collected in a gasometer over brine, or let out into the atmosphere. Through the apparatus a current of dry pure nitrogen could be passed both previous to and during the experiment. Some of the runs were carried out in vacuo; in these cases no gas sampling was done. For comparison one run was carried out without a catalyst.

For solid and liquid reaction products were determined the melting point, the bromine value (6) and in some cases the molecular weight according to Rast (as described above for the initial paraffin); from the latter figure the content of unsaturates was calculated. The contact gases were analysed with the Orsat-Jäger apparatus. Before every run the catalyst was regenerated under standard conditions by blowing air through it until the complete combustion of carbon (30 min.).

The results obtained are tabulated below. In Table 1 the regime and the quantitative relationship between the initial and the final products are given; Table 2 shows the analysis of contact gases. In Table 3 the properties of the condensates and of the initial solid paraffin are given.

The examination of the tables leads to the following conclusions:

W i t h o u t a c a t a l y s t there is almost no evolution of hydrogen, even under the most severe conditions of this work. In general very little gas is evolved and it consists chiefly of saturated and unsaturated hydrocarbons (run 7).

In c a t a l y t i c experiments, on the contrary, much gas is evolved, mainly hydrogen. Olefin are also formed in great quantities (column 4, Table 3). At

Table 1

Nos. of runs	t °C	Duration of exper., min.	Paraffin used, g	Obtained		Yield of condensate, weight %
				condensate, g	gas, l	
1	2	3	4	5	6	7
7	550	45	34.0	31.5	0.9	92.6
3	450	11.5	33.5	32.0	3.4	95.6
6	500	48	44.1	41.5	—	94.1
5	550	62	55.4	41.5	—	75.0
4	550	60	54.0	39.0	—	72.2
1	550	20	5.0	3.5	2.6	70,0
2	550	20	11.0	7.3	8.5	66.3

Notes. In runs 1—6 nitrogen was passed before and during the run. In run 2 two samples of gas were taken: in the beginning of the run, 5 l, and at the end, 3,5 l. In run 4 in the middle of the run a sample of gas was taken, 5.0 l; all the gas was not collected. In runs 5 and 6 vacuum was made by means of a water pump. Residual pressure in run 5 was 50—70 mm, and in run 6,250 mm Hg. In run 7 the system was washed with nitrogen, but during the run nitrogen was not passed; the run was carried out without the catalyst in an empty quartz tube.

Table 2

Nos. of runs	Analysis of contact gas, % by volume						
	Olefins			Saturated hydrocarbons	H_2	CO_2	N_2
	C_2H_4	higher olefins	total				
1	2	3	4	5	6	7	8
7*	28.0	25.2	53.2	36.2	3.0	0.	7.0
3	0.6	0.8	1.4	3.2	81.6	0.4	13.2
4	0.4	2.0	2.4	5.6	78.6	0	13.2
1	1.6	2.0	3.6	11.0	56.2	1.4	27.8
2 a**	0.2	1.6	1.8	9.8	77.6	1.0	9.6
2 b***	0.8	3.8	4.6	16,7	65.6	0	13.1

Table 3

Nos. of runs	Consistence, colour, melting point °C of condensate	Molecular weight, average	Bromine value	Contents of unsaturates, weight %
1	2	3	4	5
Initial paraffin	White, dry, m. p. 50° . .	554	0.94	3.3
7	Almost white, solid mass, m. p. 45-46°	—	13.3	—
3	Yellowish solid mass, m. p. about 43°	459	11.2	32.1
6	Same as in run 3, m. p. about 43	450	17.2	48.4
5	Dark brown grease like mass, m. p. 26—27°	285	32.9	58.5
4	Same as in run 5, m. p. 26—30°	—	34.6	—
1	Mobile oil coloured brown	—	33.8	—
2	Mobile transparent oil coloured red brown	—	31.4	—

* Without a catalyst. ** Beginning of run 2. *** End of run 2. In all cases O_2 not above 0.2%.

lower temperatures there is only a small decrease in molecular weight (Table 3). All condensates had a sharp smell of unsaturates. At 450° decomposition is inconsiderable, but increases rapidly with a rise in temperature (column 7; Table 1). With time the decomposition reaction increases at the expense of dehydrogenation (run 2; Table 2). We come to the conclusion that higher paraffins over the investigated catalyst undergo the following transformations:

$$\text{I. } C_nH_{2n+2} = C_nH_{2n} + H_2$$

$$\text{II. } C_nH_{2n+2} = C_6H_5 \cdot C_{n-6}H_{2n-11} + 4H_2$$

$$\text{III. } C_nH_{2n+2} = C_{n/2}H_n + C_{n/2}H_{n+2}$$

$$\text{IV. } C_nH_{2n+2} = (n-2)\,C + 2CH_4 + (n-3)\,H_2$$

Here we have the following reactions: I—dehydrogenation; II—aromatization; III—consecutive reactions of cracking, discovered by Thorpe and Young for the pyrolysis of higher paraffins in the absence of a catalyst, and IV—a reaction analogical to the one studied by us in the decomposition of butane ([7]).

Thermodynamical calculations based on the data ([8]) known up to now on the free energy of hydrocarbons (besides those participating in reaction II) showed that reaction I, III and IV at 450—550° are possible and that they become more intense with rise of temperature and with increase of the hydrocarbon chain. The complete decomposition of the paraffin according to reaction IV should dominate over other reactions.

The specific action of our catalyst consists in a different acceleration of the advance ment of these reactions towards equilibrium. Under definite conditions the acceleration of the decomposition according to reaction IV is not great.

At 450°, atmospheric pressure and space velocity of the paraffin 7.6 g/cm³/hr in run 3, from 60 mmol of paraffin were obtained 24 mmol of olefins, 111 mmol H_2 (with correction on STP) and 5 mmol CH_4 (counting saturated gases as CH_4), and the average molecular weight decreased from 554 to 459. Such results can be obtained if reactions I; II; III and IV proceed correspondingly to 20%; 2%, 20% and 4%; actually on the base of this ratio one can calculate that from 60 mmol of paraffin should be obtained 24 mmol olefins; 111 mmol H_2; 5 mmol CH_4 and the average molecular weight of the condensate should be 461; if the initial one was 562 ($C_{40}H_{82}$). This calculation is the same whether a paraffin C_n or $C_{n/2}$ is dehydrogenated. Losses in the condensate are calculated as 1.3 g against 1.5 g observed.

At 500°, a pressure of 250 mm and space velocity 2.4 g/cm³/hr from run 6 it can be found analogously that reactions I, III and IV proceed by 36, 21 and 5%.

At 550° almost twice as much olefins are formed (Table 3); but the process is complicated by the decomposition reactions that are intensified (column 7; Table 1); already a single passage of the paraffin leads to its liquefaction and the average molecular weight decreases almost to half the former value (Table 3).

Thus, at 450—500° dehydrogenation and formation of olefins prevails considerably over other reactions of the paraffin over that catalyst. The reaction products, the olefins, can be an interesting material for further syntheses. The work is being continued.

In the carrying out of this work we were helped by V. A. Klimova and R. G. Seymovitch to whom our thanks are due.

Institute of Organic Chemistry.
Academy of Sciences of the USSR.

Received
14. V. 1943.

REFERENCES

[1] T. E. Thorpe and Young, Ann., **165**, 1 (1873). [2] A. A. Balandin, N. D. Zelinsky, M. N. Marushkin and L. N. Pavlov, C. R. Acad. Sci. URSS, XXXII, 135 (1941). [3] Germ. Pat. 596094 (1934); Ch. Abs., **28**, 4430 (1934). [4] Технич. нормы на нефтепрод., изд. 9, 115 (1942). [5] Kraft, Ber., **40**, 4783 (1907). [6] А. А. Баландин, Н. Д. Зелинский, Г. М. Марукян и О. К. Богданова, ЖПХ, **14**, 16 (1941). [7] A. A. Balandin, M. N. Marushkin and M. M. Afanassiev, Bull. Acad. Sci. URSS. sér. chim., 1, No. 80 (1941). [8] C. L. Thomas, G. Egloff and L. C. Morrell, Journ. Eng. Ch., **29**, 1260 (1937); C. M. Thacker, H. O. Folkins and E. L. Miller, ibid., **33**, 584 (1941).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

CHEMISTRY

PRODUCTS OF THE REACTION OF THIOSULPHATOPLATINITES WITH CERTAIN AMINES

By D. I. RIABCHIKOV

(Communicated by A. E. Arbusov, Member of the Academy, 19. IV. 1943)

As is known, the action of certain amines—pyridine, ammonia, ethylene diamine, thiourea and others—on chloroplatinites leads in the first stage of the reaction to partial replacement of the intraspheral chlorine atoms by molecules of the amine. Moreover, in a vast majority of cases the Peironnet rule is observed, in accordance with which the molecules of the amine assume a cis-position:

$$K_2[PtCl_4] + 2Am \rightarrow \begin{bmatrix} Cl & Am \\ & Pt \\ Cl & Am \end{bmatrix} + 2KCl$$

where $Am = NH_3$, C_5H_5N, $\frac{1}{2}C_2N_2H_8$.

However, this rule is not always obeyed, and in the case of thiourea, for instance, a different isomeric form of the reaction product is obtained:

$$K_2[PtCl_4] + 2SCN_2H_4 \rightarrow \begin{bmatrix} SCN_2H_4 & Cl \\ & Pt \\ Cl & SCN_2H_4 \end{bmatrix} + 2KCl.$$

First obtained by Kurnakov (1), it has been shown by him to have trans-structure.

The cases under consideration can be explained very well in terms of the trans-influence established by Černjaiev (2). A diverse degree of the trans-influence of the diagonal partner within the internal sphere leads to a diverse type of substitution. We thought it of interest to follow the chemism of the interaction of these amines with the thiosulphatoplatinite $K_6[Pt(S_2O_3)_4]$ described by us(3).

From the peculiarity of the $S_2O_3^{--}$ ion (double charge and strong trans-influence) different circumstances complicating the reaction were to be expected in the case of thiosulphatoplatinites as compared with chloroplatinites.

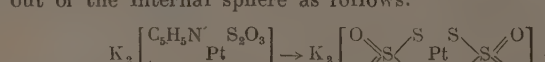
1. A solution of the salt $K_6[Pt(S_2O_3)_4]$ was heated for a protracted period of time on a water bath with an excess of pyridine. Then the solution was cooled down and the excessive pyridine removed, after which some ethyl alcohol was added, causing the formation of a yellow precipitate. Upon an analysis of this precipitate it was established that it precisely corresponded in composition to the formula $K_2[Pt(S_2O_3)_2]$.

In some of the experiments a solution of $[Pt4SCN_2H_4]Cl_2$ was added without first removing the excess of pyridine, and immediately a yellow crystalline precipitate separated out that corresponded in composition to the formula $[Pt(S_2O_3)_2][Pt4SCN_2H_4]$. Thus, as a result of the treatment of the solution with pyridine, the complex $K_6[Pt(S_2O_3)_4]$ passes into $K_2[Pt(S_2O_3)_2]$. In the first case the thiosulphate residues are linked to platinum through the sulphur atoms, in the second, by a closed cycle; taking up two coordination positions each.

The discovered phenomenon may be explained as follows. At the outset in the presence of a large excess of pyridine replacement of the thiosulphate groups of the internal sphere by molecules of pyridine takes place in the following manner:

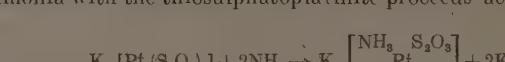
$$K_6[Pt(S_2O_3)_4] + 2C_5H_5N \rightarrow K_2\begin{bmatrix} C_5H_5N & S_2O_3 \\ & Pt \\ C_5H_5N & S_2O_3 \end{bmatrix} + 2K_2S_2O_3.$$

This mixed pyridine-thiosulphite form is very unstable; since the pyridine molecules are in the trans-position with respect to the thiosulphate fragments, and their linkage to platinum is thereby greatly weakened. At the same time the thiosulphate groups within the complex molecule have a tendency to close the cycle through the oxygen atoms. The result is that the pyridine molecules are forced out of the internal sphere as follows:



Owing to the slight stability of the cis-form of the mixed pyridine-thiosulphite compound, we did not succeed in isolating it. The chemical analogue of the trans-configuration, on the other hand, which we isolated previously ([4]), is a very stable compound. This essential difference between the two isomeric forms is explained by the position of the coordinated molecules of pyridine with respect to the thiosulphate residues.

2. The more stable coordination bond between ammonia and platinum affords the possibility of obtaining a mixed thiosulphate-ammonia compound in the cis-form. If the same initial complex salt is heated up with a saturated solution of ammonia, the initial intensely yellow colour fades. The presence of free S_2O_3-ions in the solution may be easily revealed by a barium chloride test. Interaction of the ammonia with the thiosulphatoplatinite proceeds according to the following scheme:



The strict observance of the Peironnet rule in the case of ammonia as well as pyridine is due to the fact that the antagonistic influence of the trans-partner in any thiosulphate group is eliminated as soon as an ammonia molecule is fixed at the diagonally opposite end.

The system $S_2O_3^{=}$—NH_3 proves to be many times as stable as $S_2O_3^{=}$—$S_2O_3^{=}$, where the mutual trans-influence of the acid residues weakens their linkage with the nucleus of the complex. In the combination $S_2O_3^{=}$—$S_2O_3^{=}$ the second molecule of ammonia will therefore only replace the thiosulphate residue. Regardless of which of the thiosulphate groups is replaced by a molecule of ammonia, the second molecule of ammonia is in a cis-position with respect to the first just the same.

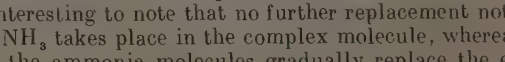
From an ammonia solution to which a solution of the salt $[Pt4SCN_2H_4]Cl_2$ has been added, there precipitates a sparingly soluble crystalline salt of a light cream colour, which; upon analysis, is found to correspond in composition to the formula: $[Pt2NH_3(S_2O_3)_2]$ $[Pt4SCN_2H_4]$. After filtering off from such an ammonia solution the BaS_2O_3 precipitate that is separated out by the action of a calculated quantity of $BaCl_2$; in response to treatment ethyl alcohol precipitates yellowish flakes of a barium salt.

Analysis. Calculated for $Ba[Pt2NH_3(S_2O_3)_2]$: Pt, 33.04%; Ba, 23.24%; H, 4.73%. Found: Pt, 33.10%; Ba, 23.34%; H, 4.30%.

The somewhat larger electrical conductivity and solubility of the cis-isomer of the barium salt $Ba[Pt2NH_3(S_2O_3)_2]$ that was obtained distinguish it noticeably from the trans-isomer previously described by us ([5]).

It is interesting to note that no further replacement not even of one more $S_2O_3^{=}$ group by NH_3 takes place in the complex molecule, whereas in the case of halogen platinites the ammonia molecules gradually replace the entire internal sphere of the complex.

3. A still more stable mixed thiosulphate compound is found by ethylene diamine which adds to in a closed cycle. The reaction which was effected under similar conditions, took place in this case according to the scheme:



The very fact of the replacement of adjacent thiosulphate groups by a molecule of ethylene diamine is proof that compounds, forming as a result of the action of amines on platinum thiosulphates, have a cis-structure.

Ethyl alcohol precipitates an oily liquid which is a mixture of $K_2S_2O_3$ with the product formed. The latter, dissolving very well in water from the alcoholic mother liquid, after standing for a protracted period of time separates out as a light-cream coloured voluminous precipitate composed of long fibres. The composition of the compound corresponds to the formula $K_2[PtN_2C_2H_8(S_2O_3)_2]$.

The composition of the anion was established on a compound forming as a result of an exchange reaction with the Reise 1 salt according to the scheme

$$K_2[PtN_2C_2H_8(S_2O_3)_2] + [Pt4NH_3]Cl_2 \rightarrow [PtN_2C_2H_8(S_2O_3)_2][Pt4NH_3] + 2KCl.$$

Analysis. Calculated for $[PtN_2C_2H_8(S_2O_3)_2][Pt4NH_3]$: Pt, 52.55% and N, 11.31%. Found: Pt, 52.68% and N, 11.08%.

4. In all the cases considered above, the interacting amine effected its linkage to the central atom of the complex through the nitrogen atom. Such linkage did not give rise to any anomalous phenomena whatever in the complex molecule. Here Černjaiev's effect is meant. Thiourea, on the other hand, like the transthiosulphate residue, gives a maximum effect.

As was already pointed out, NH_3, C_5H_5N, as well as $N_2C_2H_8$, once in the internal sphere of the complex, facilitate the attachment of the remaining thiosulphate residues. The thiourea does not change position. The thiosubstitutes antagonistically affect one another to a like degree. In practice upon the addition of thiourea to a solution of $K_6[Pt(S_2O_3)_4]$ as well as to the other thiosulphatoplatinites isolated [3], the solution first becomes turbid very rapidly, and immediately afterward a curdy precipitate settles down which when left standing for a long time (several days) in the mother liquor, crystallizes out into long yellow prisms. The precipitate is practically insoluble and corresponds in composition to the formula

$$[Pt3SCN_2H_4 \cdot S_2O_3].$$

Attention is called to the following circumstance; namely, that a precipitate of this composition is formed no matter what the proportion of thiourea added. As a result of the reaction an unstable equilibrium is set up in the solution:

$$K_6[Pt(S_2O_3)_4] + 2SCN_2H_4 \rightleftarrows K_2[Pt2SCN_2H_4(S_2O_3)_2] + 2K_2S_2O_3.$$

The mixed salt formed in the solution as either cis- or trans-form, both being equally possible, reacts with a third molecule of thiourea, whereby a non-electrolyte is formed:

$$K_2[Pt2SCN_2H_4(S_2O_3)_2] + SCN_2H_4 \rightarrow [Pt3SCN_2H_4S_2O_3] + K_2S_2O_3.$$

This salt, being sparingly soluble, is carried down. The last $S_2O_3^{=}$ group is very firmly held in the internal sphere of the complex; and we did not succeed in replacing it with either thiourea or any other molecule.

Conclusions. 1. The Peironnet rule which calls for the formation of a cis-isomer upon the action of an amine on a chloroplatinite, also holds in the case of thiosulphatoplatinites, but there is a certain deviation with amines of the pyridine type whose coordination bond is less firm.

2. Thiourea, on the other hand, is an exception here also and leads to the formation of a triamine in which the last $S_2O_3^{=}$ group cannot possibly be replaced.

3. Products of the interaction with amines of cis-configuration were isolated and found to have the following composition:

$$Ba[Pt2NH_3(S_2O_3)_2];\quad [Pt2NH_3(S_2O_3)_2][Pt4SCN_2H_4];$$
$$K_2[PtC_2N_2H_8(S_2O_3)_2];\quad [PtC_2N_2H_8(S_2O_3)_2][Pt4NH_3].$$

Institute of General and Inorganic Chemistry.
Academy of Sciences of the USSR.

Received
19. IV. 1943.

REFERENCES

[1] Н. С. Курнаков, Собр. избр. работ, I, 68 (1938). [2] И. И. Черняев, Изв. Ин-та платины и др. благород. мет., вып. 5 (1927). [3] D. I. Riabchikov, C. R. Acad. Sci. URSS, XXVII, No. 4 (1940). [4] D. I. Riabchikov, ibid., XXVII, No. 7 (1940). [5] D. I. Riabchikov, ibid., XXVIII, No. 3 (1940).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

PHYSICAL CHEMISTRY

ON THE CRYSTAL CHEMISTRY OF THE LAVES PHASES

By G. B. BOKY and E. E. WAINSTEIN

(Communicated by V. G. Chlopin, Member of the Academy, 12. V. 1943)

1. Among the intermetallic compounds which do not fit within the scope of the classical ideas on valency, some authors set apart a relatively small group of compounds under the name of phases of Laves who was the first to study them (1). These compounds are characterized by a formula of the shape AB_2 or $AB_x B'_{2-x}$ and by a definite type of their crystalline structure.

The compounds actually known as «Laves phases» are:

$CuBe_2$, ZrW_2, $TiCo_2$, $MgNi_{1.8}Si_{0.2}$, MgNiZn, $PbAu_2$, $AgBe_2$, KBi_2, $NaAu_2$, $CaAl_2$, $FeBe_5 = (FeBe)Be_4$, WFe_2, $FeBe_2$, $TiFe_2$, VBe_2, $CaMg_2$, WBe_2, MgCuAl, $MgCu_{1.5}Si_{0.5}$, $MgNi_2$, $Mg(ZnCu)_2$ etc.

Classing the Laves phases as a separate group of intermetallic compounds, Schulze infers therefrom for the electronic structure of their atoms a uniform scheme accounting for the type of the chemical bond. He overlooks, however, the following fact:

1) Both these characters, viz. the identity of the crystalline structure and of the type of the chemical bond within the limits of a single group, are independent of each other, and one of them cannot always be univocally determined by the other.

2) Either of these characters does not always suffice to characterize a group. Thus, the difference in the character of the chemical bond in the following compounds is quite obvious: NaCl—MgO—MnSe—PbTe—SnSb, each of which crystallizes according to the structural type NaCl. A still better illustration is supplied by rare gases and noble metals which are crystallized as structures with a cubic face-centred lattice.

2. The structures of Laves phases are characterized by coordination numbers (12, 6) but, unlike usual coordination lattices, the *B*-atom will have six *B*-atoms as its closest neighbours. And this accounts for the fact that similar structures are not observed in ionic compounds. These structures are essentially different from the coordination structures in that two independent lattices of components inserted in each can be distinguished in them (Schulze's «Teilgitter»). Structures of this kind permit of no variation in the magnitude of the relation between the radii of the components. At the moment which corresponds with the contact of uninomial spheres, the ratio between radii $R_A : R_B = \sqrt{3}\,\frac{a}{8} : \sqrt{2}\,\frac{a}{8} = 1.225$, and distance $d_{AB} = \sqrt{11}\,\frac{a}{8}$. In the structures of Laves phases practically observed till now the values for the ratio between the radii of the components are grouped around a value corresponding to the ideal structure with incompressible spheres (1.225), though it may deviate from the latter within the range of 1.11—1.33*.

* Schulze gives for $CaAl_2$ ratio $R_A/R_B = 1.38$. However, if instead of the $d_{AA/2}$ and $d_{BB/2}$ from structures, atomic radii are used, then this relation will be 1.31.

In his work Schulze arrived at a conclusion that the polarization of atoms plays no important rôle in these structures, and that the formation of Laves phases cannot be put down to polarization properties. We cannot agree with this assertion. The rôle played by polarization in Laves phases is a material one. If we consider a highly polarizable metal atom as a sphere which under the influence of its neighbours is apt to structural variation without appreciably changing its volume [2], then for limit cases it is possible to calculate values of the «radii» A and B of the components in the Laves phases $\left[R'_A = (\sqrt{11} - \sqrt{2})\ \frac{a}{8},\ R'_B = (\sqrt{11} - \sqrt{3})\frac{a}{8}\right]$. Hence for $R'_A : R_B$ and $R_A : R'_B$ the respective magnitudes 1.09 and 1.34 are obtained. The good agreement between the calculated magnitudes of the relations of atomic radii and those experimentally observed makes us believe that a real atom is not capable of infinite deformation, but, after having encountered obstacles in 12 points (as, e. g., in the case of B-atoms), or in 16 points (A-atoms), is capable of no further deformation.

3. The important part belonging to mutual polarization of components in the compounds of the Laves type may sometimes be disguised by the influence of individual characters of the electronic structure of the atoms they are made of. It is expedient to class all the elements that participate in the formation of Laves phases into three groups: a) elements met as A-components only (Na, K, Ca, Ti, Ag, Pb, V, Cr, Mo, Re); b) elements that occur only as B-components (Zn, Be, Co, Ni and Al); c) such as occur both as A and B-components (Mn, Fe, Cu, Au, Bi and Mg). It should be kept in mind that the geometry of Laves phases excludes, for instance; for Be, Co and Ni the possibility of operating as A-components; it does not permit Na, K and Ca either to form Laves phases in which they would play the rôle of B-components. When trying to explain the mechanism of formation of Laves phases, allowance should be made for the possible «percolation» of the peripheral electrons of one of the components into the deficient shells of the transition element which, as a rule, plays the part of one of the components in the Laves phases. It is necessary, however, in this case to give up the requirement arbitrarily postulated by Schulze, viz. that the donor of electrons in the compound should necessarily be the A-component, which is by no means obligatory for metallic lattices. We thus get rid of the necessity of assuming (as does Schulze) a number of artificially excited states of the atoms forming the B-components. The consequences which follow from our assumption are in good agreement with the changes observed in the radii of both components, when the atoms they are made of enter the Laves phases. From this point of view especially illustrative is the most abundant series, that of AB_2 compounds.

4. The attempt to give the redistribution of electronic charge between the A and the B-components in the Laves phases, as well as the attempt to characterize Laves phases by a definite value of electronic density, as made for the Hume-Rosery phases, proved a failure, because of the roughness of the theory. Unlike the Hume-Rosery phases, Laves phases represent no homogeneous group and may possibly include a number of super-structures. Thus, the experimental and theoretical material available on the crystal chemistry of Laves phases does not permit at the time being to regard them as an independent group of intermetallic compounds. The term of «Laves phases» may be applied only to a definite type of crystalline structures.

To conclude; it is a pleasure heartily to acknowledge the help of Dr. B. N. Delaunay in this work.

Institute of General and Inorganic Chemistry,
Academy of Sciences of the USSR.

Received
18. V. 1943.

REFERENCES

[1] F. Laves, ZS. f. Krist., 73, 248 (1930). [2] G. B. Boky and E. E. Wainstein, Bull. Acad. Sci. URSS, sér. chim., No. 4 (1943).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

PHYSICAL CHEMISTRY

KINETICS OF ISOTHERMAL COAGULATION OF NOT COLLIDING PARTICLES

By N. N. SIROTA

(Communicated by N. P. Chizhevsky, Member of the Academy, 13. III. 1943)

Let us consider the question of isothermal coagulation of not colliding particles when the following conditions are imposed. A solid dispersion phase I is dispersed in the form of spheroidal particles (crystals) inside a solid matric phase II. The quantity of the dispersion phase remains constant throughout the process.

Any convertion currents are entirely absent from the system; and there is no transfer of, or collision between, particles. The matric phase is near in its properties to an isotropic medium; its diffusion velocities are equal in all directions.

It may dissolve in itself a certain amount of the dispersion phase.

In this ideal case the coagulation may be regarded as a cumulative process made up of two elementary processes—the dissolution of particles (crystals) of the dispersion phase, and their growth. As an average, the finer particles dissolve more rapidly than they grow, whereas the dissolution of the coarser particles is less rapid than their growth. To characterize the process as a whole, one may speak of an increase of the average size of particles in time, the coarse particles growing at the expense of the fine. And at any given moment a boundary may be easily drawn between the relatively coarse and fine particles. In other words, it is possible to show the existence of such a mean effective size when the rate of dissolution is equal to that of growth. It is obvious, however; that this boundary is apt to shift in the course of time, so that the next moment another average size of the particles will be established; since the coarser crystals gradually increase in size, while the finer ones partly vanish and decrease in number.

Suppose that when the isothermal process of coagulation is established, the distribution of the particles of the dispersion phase according to size at any given moment t and at a temperature T can be described by the distribution function of the Gauss type.

This function may be approximated by the expression (1)

$$\frac{dZ}{ds} = As^p e^{-\alpha s}, \qquad (1)$$

Here A is normalizing factor; α is a parameter, depending upon temperature and time; z is the number of particles in one grammole of the disperson phase; s is the surface area of one particle.

To simplify the problem, we put $p=3$; this, in reality, corresponds to a great number of actually observed cases.

The condition for the constancy of mass of the dispersion phase I in a unit volume of the matric phase II makes it possible to determine the value of the

normalizing factor A. For one grammole M of the dispersion phase I one may write the equation:

$$M = \int_0^\infty m n_s \frac{dZ}{ds}\, ds, \tag{2}$$

where m is the mass of an atom (a molecule); n_s the number of atoms (molecules) in a particle with the surface area s.

It is evident that $n_s = \frac{s^{3/2}}{c^{3/2}}$; here we have $c = k_s \left(\frac{M}{\rho N}\right)^{2/3}$, where ρ is density of the dispersion phase; N is the number of atoms in a grammole; k_s is the coefficient of shape; for spheroidal particles $k_s = (36\pi)^{1/3} = 4.83$.

Substituting in (2) the respective values for n_s and $\frac{dZ}{ds}$ and integrating over all the possible dimensions of the surface area of the particles, we find the value of A:

$$A = \frac{Mc^{3/2}}{m} \frac{\alpha^{p+2.5}}{\Gamma(p+2.5)} = \eta \frac{\alpha^{p+2.5}}{\Gamma(p+2.5)} \tag{3}$$

where $\eta = \frac{Mc^{3/2}}{m} = 6\pi^{1/2} V = 10.6V$, V being the volume of one grammole of the dispersion phase.

Here and in the following the critical value of three-dimensional nuclei δ_3 is not taken into consideration, but is supposed to be zero.

For the number of particles Z_t in one grammole of the dispersion phase we write the equation:

$$Z_t = \int_0^\infty \frac{dZ}{ds}\, ds = \eta \frac{\Gamma(p+1)}{\Gamma(p+2.5)} \alpha_t^{1.5}. \tag{4}$$

Accordingly, we have

$$Z_t - Z_0 = -\Delta Z = \eta \frac{\Gamma(p+1)}{\Gamma(p+2.5)} [\alpha_t^{1.5} - \alpha_0^{1.5}] \tag{5}$$

where the subscripts correspond to the initial t_0 and ultimate t value of the time t.

Similarly, for the total area of the interface we write

$$S_t = \int_0^\infty s \frac{dZ}{ds}\, ds = \eta \frac{\Gamma(p+2)}{\Gamma(p+2.5)} \alpha_t^{0.5} \tag{6}$$

and, respectively,

$$S_t - S_0 = \eta \frac{\Gamma(p+2)}{\Gamma(p+2.5)} [\alpha_t^{0.5} - \alpha_0^{0.5}]. \tag{7}$$

The mean arithmetical value of the surface area of the crystals in a grammole of the dispersion phase is

$$S_{\text{mean arithm}} = \frac{S_t}{Z_t} = (p+1)\alpha^{-1}. \tag{8}$$

It will be apparent that the mean effective value of the surface area of the crystals is

$$S_{\text{mean}} = \varkappa^2 \alpha^{-1}, \tag{8a}$$

where $\varkappa$ is a constant depending upon p.

The concentration C of the solid solution of the matric phase II at the boundary with the dispersion phase I varies with the dispersion of the particles of the phase I and may, as an average, be expressed by the mean

effective value of the surface area of the particles S_{mean} on the basis of Thompson's equation:

$$C_{mean} = C_\infty e^{k_1 S_{mean}^{-1/2}} \tag{9}$$

or, if S_{mean} is expressed by the parameter α, we in virtue of equation (8a) obtain

$$C_{mean} = C_\infty e^{k_1 \sqrt{\frac{\alpha}{\varkappa^2}}}. \tag{9a}$$

C_∞ is equilibrium concentration of the phase II on the boundary with infinitely large crystals of the phase I, as determined from the constitution diagram; k_1 is a constant. According to Thompson's equation $k_1 = \frac{4\sqrt{\pi} M\sigma}{\varrho RT}$, where σ is surface energy at the interphase.

In order to determine $S_{mean\ eff}$ we have to solve the equation

$$C_{mean_t} = \frac{C_\infty \int_{s_3}^{\infty} e^{\frac{k_1}{\sqrt{s}}} ds}{Z_t} = C_\infty e^{\frac{k}{\sqrt{S_{mean}}}}.$$

We shall not solve this equation, however, and for determining $\varkappa$ shall make use of the following method.

The change of free energy in the system ΔF in course of coagulation, due to the change of the internal surface area, may likewise be expressed by the parameter α. This change is*

$$F_t - F_0 = RT \ln \frac{C_{mean_t}}{C_{mean_0}} = RT \frac{k_1}{\varkappa} (\alpha_t^{0.5} - \alpha_0^{0.5}). \tag{10}$$

The change of the free energy of the dispersion system in the process of isothermal coagulation varies directly as the product of the surface energy σ by the change of the internal surface area $S_t - S_0$. In fact

$$RT \frac{k_1}{\varkappa} (\alpha_t^{0.5} - \alpha_0^{0.5}) = k_2 \sigma (S_t - S_0),$$

where $k_2 = \frac{2}{3} \frac{\Gamma(p+2.5)}{\varkappa \Gamma(p+2)} = 1$. From the condition $k_2 = 1$ we find $\varkappa = \frac{2}{3} \frac{\Gamma(p+2.5)}{\Gamma(p+2)}$.

The time variations of the nuantities Z_t, S_t, S_{mean}, ΔF, which are the most important for us as they determine the condition of the dispersion system, are expressed by the parameter α. Hence, it suffices to determine the variation of any of these quantities with time in order to find the time variation of the parameter α; in this way the change of all the remaining values with time can be determined.

The variation of the number of the particles of the dispersion phase I with the time is found on the basis of the following considerations.

In course of an isothermal coagulation the dissolution of fine particles smaller in size than S_{mean} and the disappearance of the particles whose size is below that of the three-dimensional nuclei is not offset practically by the formation of new particles. Therefore the change in the total number of the system particles during the interval $\Delta t = t - t_0$ will correspond to the total number of crystals that existed at the initial moment t_0, and could be reduced during the interval Δt to the size of three-dimensional nuclei and vanish.

---

* A more correct way with expressions (9), (9a), (10) is to use activities instead of concentrations.

Let S_x correspond to the surface area of the largest particles that disappear during this interval. Then the total change of the particles during the interval Δt is:

$$\Delta Z = \int_0^{S_x} As^p e^{-\alpha s}\, ds = \eta \frac{\Gamma(p+1)}{\Gamma(p+2.5)} \alpha_0^{1.5} \{e^{-\alpha_0 S_x}(\alpha_0 S_x + 1)^p - 1\} =$$

$$= Z_0 \{e^{-\alpha_0 S_x}(\alpha_0 S_x + 1)^p - 1\}. \qquad (11)$$

It is obvious that the change of the number of particles of the dispersion phase I during the interval Δt depends upon the exponent p which characterizes the curve of distribution of particles according to size. For $p=3$ we have

$$\Delta Z = Z_0 - Z_t = \int_0^{S_x} As^3 e^{-\alpha s} ds = Z_0 [e^{-\alpha_0 S_x} - 1]^3. \qquad (11a)$$

On the other hand, if follows from the relation (5) that the change of the total number of particles during the interval Δt may be expressed by the parameter α which depends upon time. Equating the expression (5) and (11), the time variation of the parameter α can be expressed by the time variation of S_x.

In accordance with the diffusion theory, the surface area of the dissolving particle changes during the interval dt by as much as

$$ds = -\mu D (C - C_{\text{mean}})\, dt, \qquad (12)$$

where D is coefficient of diffusion; μ is a constant, determined by the relation $\mu = \frac{8\pi a}{\rho}$ where a is the mass of the dissolved substance of the dispersion phase I in the phase II for $C=1$; ρ is density of the dispersion phase.

Making use of the relations (9) and (9a); the expression (12) can also be written in a different form:

$$ds = -\mu D C_\infty (e^{\frac{k_1}{\sqrt{S}}} - e^{\frac{k_1}{\chi}\sqrt{\alpha}})\, dt. \qquad (12a)$$

In order to find the value S_x, we have to integrate the differential equation (12), and obtain

$$\int_{\alpha_0}^{\alpha_t}\int_0^{S_x} \frac{d\alpha\, ds}{e^{\frac{k_1}{\sqrt{S}}} - e^{\frac{k_1}{\chi}\sqrt{\alpha}}} = -\int_{t_0}^{t} \mu D C_\infty dt = -\mu D C_\infty \Delta t. \qquad (13)$$

As under real conditions $\frac{k_1}{\sqrt{S}}$ and $\frac{k_2}{\chi}\sqrt{\alpha}$ are less than unity, we find, after the exponential function $e^{\frac{k_1}{\sqrt{S}}}$ is developed in a series in which all terms but the first two are neglected, that

$$S_x = \left[\frac{3}{4} \frac{k_1 \mu D C_\infty \Delta t}{\alpha_t - \alpha_0}\right]^{2/3} = \left[\frac{3}{4} k_1 \varphi^{2/3} \frac{\mu D C_\infty \Delta t}{Z_t^{2/3} - Z_0^{2/3}}\right]^{2/3}; \qquad (14)$$

where $\varphi = \eta \frac{\Gamma(p+1)}{\Gamma(p+2.5)}$.

Substituting in (11a) the approximate value of S_x thus obtained; we shall have

$$\left(\frac{Z_t^{2/3} - Z_0^{2/3}}{Z_0}\right) \ln\left[1 - \left(\frac{\Delta Z}{Z_0}\right)^{1/2}\right] = -(\vartheta \Delta t)^{2/3}, \qquad (15)$$

where $\vartheta = \frac{3}{4} k_1 \varphi^{2/3} \mu D C_\infty = 5.31 \varphi^{2/3} \mu V \frac{D C_\infty \sigma}{RT}$.

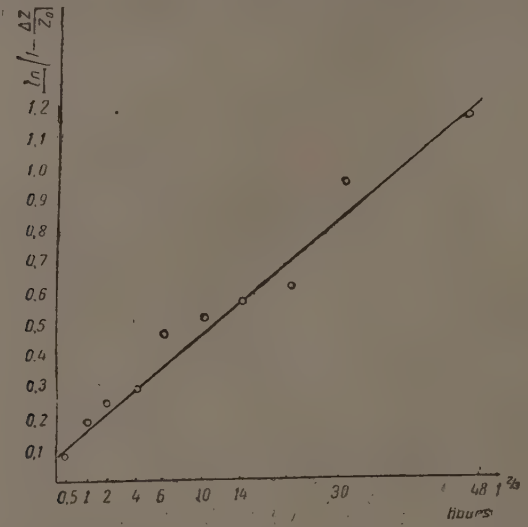
The duration of the coagulation process for a given variation of the number of particles is:

$$\Delta t = \frac{1}{\vartheta} \frac{Z_0^{2/3} - Z_t^{2/3}}{Z_0} \ln^{2/3} \left[1 - \left(\frac{\Delta Z}{Z_0} \right)^{1/2} \right]. \qquad (16)$$

Simplifying the solution and taking approximately that

$$\left(\frac{Z_0^{2/3} - Z_t^{2/3}}{Z_0} \right) \ln \left[1 - \left(\frac{\Delta Z}{Z_0} \right)^{1/2} \right] \approx \ln \left[1 - \frac{\Delta Z}{Z_0} \right],$$

we find, as first approximation, the expression for the change of the number



of particles ΔZ during the interval Δt in the process of isothermal coagulation:

$$Z_0 - Z_t = Z_0 (1 - e^{-\vartheta^{2/3} \Delta t^{2/3}}). \qquad (17)$$

This approximate expression clearly reveals the rôle of the different factors (C_∞, D, σ, Δt) controlling the coagulation process. However, in estimating the rôle of these factors, the interconnexion existing between them should be taken into account.

It it evident that if the temperature dependence of C_∞, D, σ is substituted in (17), there will be obtained the dependence of the rate of the coagulation process upon the temperature.

In the figure the coordinates $\ln\left(1 - \frac{\Delta Z}{Z_0}\right)$ and $t^{2/3}$ bring out the dependence of the change in the number of carbid particles in a hardened carbon steel (experimental data) upon the time of tempering at 700°C. These data have been derived from the experimental data of Esser and Shimura (1)*. When the number of particles seen on the plane of the thin-section was recalculated with reference to the respective volume, we assumed that the ratio of these values is proportional to the radius of the particles. The recalculation was made according to the formula $Z_{\text{flat}} = k (Z_{\text{volume}})^{2/3}$. From the adjoining graph it may be seen that the experimental points fit well onto a straight line, which is a confirmation of the correctness of the expression (17).

Received
22. V. 1943.

REFERENCES

1 Shimura u. Esser, St. u. Eis., H. 48, 1674 (1930).

* Steel composition: C, 0,97; Si, 0,12; Mn, 0,12; P, 0,010; S, 0,010.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

GEOLOGY

GEOLOGICAL EVIDENCE FAVOURING THE SEARCH FOR IRON-NICKEL ORES OF THE ANATOL TYPE IN THE MIDDLE URALS

By B. P. KROTOV

(Communicated by W. A. Obruchev, Member of the Academy, 23. XII. 1942)

The iron-nickel ore deposits; belonging to the class of weathering deposits, are at present one of the most important types of deposits of these ores; they are used with equal success both for the production of metallic nickel, and for smelting ferronickel and nickel steel.

Among such deposits one of the most valuable types is presented by the Anatol type, or that of deposits of the cementation zone of the weathering crust of serpentines. To the same type in the Middle Urals refers also the Kalinychev deposit in the Verkh-Neiva district. These deposits are irregularly shaped and of variable size; and fill depressions on the surface of serpentine massifs.

The deposits of the Anatol type have been encountered among such serpentine massifs that, while being of considerable length in a nearly meridional direction, are distinguished by their relatively large size also in the latitudinal direction. Thus, the Nizhne-Taghil ultra-basic rock massif stretches for over 150 km, the width of the serpentine belt here reaching 7.5 km, and occasionally 10 km. The Verkh-Neiva massif extends for 30 km, the width being up to 20 km.

It is of interest to note that in the region of the deposits the fracturing in the serpentines follows different directions, linearly stretched zones of compression and crushing being absent.

These massifs of serpentinized peridotites with iron-nickel ores of the Anatol type form a part of a wide belt of these rocks, which stretches in a nearly meridional direction along the eastern slope of the Urals and is situated directly eastward of the central crystalline axis of the Urals. Within this belt there are a number of other massifs of serpentinized peridotites of considerable size in which as yet no iron-nickel ore deposits of the Anatol type are known; these are the Verkhne-Taghil, Verkhne-Ufalei, Turgoyak-Syrostan and other massifs.

During the Mezocenozoic in the Urals repeatedly occurred epeirogenic oscillations which produced repeated elevations and subsidences of the surface; but the sea approached the immediate vicinity of the range only towards the close of the Upper Cretaceous and the beginning of the Tertiary. At this time only the western part of the present eastern slope of the Urals remained uncovered by the sea. The belt of serpentinized peridotites, within which lie the iron-nickel ore deposits of the Anatol type in the Middle Urals, was not even once flooded by the sea during this period and remained dry land throughout. During the Mesocenozoic they were subject to weathering processes, and only in some places they were covered by continental sediments.

At present the serpentinized peridotites of the said belt with iron-nickel ore deposits project in the form of a meridional ridge whose highest points reach 423 m abs. height in the region of the Anatol deposit, 542 m (Visyachiy Kamen) in the region of the Kalinychev deposit, 564 m (B. Kamen) in the Ufalei massif.

So far iron-nickel ore deposits have been found only in the highest portions of the relief of this ridge, namely, the Anatol deposit lies at the abs. height of 365—375 m; and the Kalinychev of 470—475 m. Along the serpentine ridge in question there are also lower areas; where it is crossed by rivers flowing in a latitudinal

direction: the Chusovaya; at an elevation of 291 m; the Tura; upstream of the Vanyushina village, about 150 m; the Kyshtym, 280 m; the Kiolim; 295 m.

Geological mapping; search and prospecting for gold, chromite; iron and nickel ores, carried out in the recent years within the belt of serpentinized peridotites, have shown that the massifs of these rocks in the lower portions over a considerable area of their development are covered with a mantle of areno-argillaceous and rubbly alluvium; the age of which has not been as yet established with sufficient precision and which is generally referred to post-Tertiary deluvial deposits. Only the highest portions of the relief of the serpentinized peridotite belt lying above the 350 m abs. elevation contour, and some outcrops of peridotites, pyroxenites and gabbro, projecting in the form of knobs among the alluvium, remained uncovered. On the most elevated parts of the serpentine ridge the alluvium occurs only in depressions on their surface and is generally represented only by brown loams. The gradual increase in thickness of the alluvium when going from the summits to the river valleys and marshy lows shows that the ancient relief of the surface had been much sharper and was gradually smoothed and levelled by the alluvium.

At present the difference in the relative height between the water level in the rivers and the highest points of the serpentinized peridotite ridge attains 200 m (the level of the Neiva river at the Gaievo village is 220 m abs. height) in the southern portion of the Nizhne-Taghil massif.

The deposits of the cementation zone of the weathering crust are formed on relatively smooth surface; where the waters had no drainage at all or only a very slight one on the surface. They do not form where the water runs off speedily.

The fact that a number of known deposits occur at the absolute elevation of 360—380 m and higher; enables us to consider all of them as having been formed approximately on the same level and hence occurring now approximately on the same level after a series of epeirogenic oscillations. This justifies us in expecting their possible discovery on the same level at other places as well. The weathering deposits could have been formed on a nearly level surface and at a lower absolute elevation of the country, but such deposits ought to have been to a greater or lesser extent eroded in the pre-Quaternary time or hidden under more recent deposits. In the Anatol deposit it has been established that the deepest working; sunk to the depth of about 22 m; have not completely penetrated the ore body. Likewise, in the Kalinychev deposit the mineralization has been discovered down to the depth of 33 m (437 m abs. elevation), but here, too; the workings have not completely penetrated the ore body. Hence it follows that under the alluvium in the recent river valleys and lows; situated at the abs. elevation of about 200—220 m, there is little promise to encounter iron-nickel deposits; since they have been probably removed by later erosion.

In addition we should bear in mind that the deposits known at present (the Anatol and the Kalinychev) were subject to partial erosion during the pre-Quaternary time, and the upper portions of the ancient relief of the surface; along with the upper parts of the deposits, have been already removed by erosion.

Particularly characteristic is the geomorphology of the surface in the immediate vicinity of the deposits of the Anatol type. They are located in shallow depressions of a round or elongated shape and are surrounded on all sides by more elevate areas of serpentinized peridotites rising over the depression up to 10—15 m, and turned to rubble on the surface. These low areas are covered by humid or hillocky marshes. The erosional processes sometimes produce a wash-out of such an originally closed depression and the appearance of small gullies which subsequently drain it. A slightly pronounced slope is noted also in the Anatol deposit, where a slight inclination to the north has developed in the eastern part of the deposit.

The time of erosion in some places is referred to the Mesozoic, and in others to the Tertiary or Quaternary. The eroded surface of the serpentines and their weathering crust in a number of places have been covered later on by younger sediments. In the Kalinychev and Anatol deposits they refer to the Quaternary.

The processes of erosion have been displayed also in the South Urals deposits of a similar type, studied by I. I. Ginsburg, I. I. Saveliev, A. A. Katz, I. Z. Korin (1). Thus, according to Saveliev and Katz the Kempirsai and Shelekhta deposits are cut by small gullies filled with Jurassic and Miocene deposits. In the South-Kempirsai deposits (Spornoye and Gigant), according to the data of A. A. Filimonova and D. N. Kofanov, the weathering crust of a composition similar to that in the Anatol deposit is overlain by Upper Cretaceous marine deposits. The character of the relief on the accompanying maps shows that the weathering crust had been washed by meteoric waters, and at a later time the gullies formed with an elevated basis of erosion were filled with sediments which partly covered also the deposits themselves. According to Saveliev's data, a similar geological structure of the region of nickel-ore deposits is observed in a number of other deposits of these ores in the South Urals.

The formation of the rounded or trough-like depressions described above, in which there are found the iron-nickel ore deposits of the Anatol type, is due to weathering processes which caused the magnesium oxide and part of the silica to pass into solution and to be imbibed in the upper horizons of the fractured serpentines. The removal of these substances produced a decrease in the volume of the remaining mineral masses and their sinking down.

The removal of silica from serpentines and their alteration products brings about the appearance of quartz stringers and of various-shaped accumulations of a reddish quartz-like rock, which occur in the upper horizons of the ore body of the Anatol type deposits. Particularly typical are white quartz stringers of variable thickness in the ochre zone and the underlying zone of nontronitized serpentines. As a result of the course of joint weathering; on the surface of the deposits of this type there accumulate fragments of quartz stringers and quartzite-like mass, and sometimes the deposits are even covered with a real placer consisting of these fragments. The quartz stringers have a very characteristic structure, symmetrical on the two sides, while the quartzite-like rock has a flow structure enabling it to be readily distinguished during the search.

The geological evidence given above was used by the author as a basis in organizing the quest for iron-nickel ores in the region of the Anatol deposit in 1942 and yielded good results. Thus, at present the following geological evidence and guidind features to be used when organizing search for iron-nickel ores of the Anatol type may be indicated:

1. Quest should be organized in the first place within the belt of serpentinized peridotites, stretching along the eastern slope of the Urals, directly adjoining the central crystalline axis (the Nizhne- and Verkhne-Taghil, Verkh-Neiva, Poldnevsky, Verkhne-Ufalei and Teplogorsky massifs).

2. Search should be started on the bigger massifs of these rocks above 350 m abs. elevation in those places, where they are not covered by Mesocenozoic deposits.

3. Search should be started in those areas of serpentinized peridotites where they are distinguished by the absence of sharply pronounced zones of shearing and crushing in a meridional direction.

4. As guiding feature for search in these regions serves in the first place the geomorphology of the surface; the promising areas for organizing quest are closed and semi-closed depressions in the higher parts of the relief, surrounded by ridges and covered by hillocky meadows or bogs.

5. Another guide is the presence on the surface or in the soil of rubble or talus consisting of fragments of quartz stringers or quartzite-like rock of a flow nature.

Institute of Geological Sciences.
Academy of Sciences of the USSR.

Received
5. I. 1943.

REFERENCES

[1] А. А. Филимонова и Д. Н. Кофанов, И. И. Савельев, А. Л. Кац, Труды Ин-та геологич. наук АН СССР, вып. 49 (1941).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

GEOLOGY

KUZNETSK SERIES AT THE EASTERN LIMB OF THE KEMEROVO SYNCLINE

By V. I. YAVORSKY

(Communicated by P. I. Stepanov, Member of the Academy, 19. XII. 1942)

The classical exposures of the Permian and Jurassic coal-bearing sediments developed within the Kuznetsk basin, and of the underlying deposits of an earlier period, emerging along the banks of the Tom river, furnish a most abundant material for their investigation.

In spite of the repeated visits of scientists and travellers to the places of these exposures, the material available is still far from being thoroughly studied, so as to show all the details of the geological structure of the deposits developed here. So far there exists no detailed description, for instance, of the unique exposures of the Carboniferous and the Lower Permian along the banks of the Tom river between the village of Podyakova and the town of Kemerovo. It seems therefore interesting to give a brief preliminary characteristic of one of those regions.

An analysis of the lithological composition of the coal-bearing deposits developed in the Kuznetsk basin and of the fauna and flora enclosed therein made it possible as early as in 1940 (1) to give a considerably more detailed scheme of their stratigraphic subdivision. At present this scheme appears to be as follows.

Age	Series	Thickness in m	Coal occurrence		Carbon ratio	Notes
			Number of workable beds	Total thickness in m		
			no less	no less		
J_1	Conglomerate	650	than 12	than 13	2	With coal deposits
T_3	Malzevsky	350	—	—	—	No coal
P_2	Yerunakovsky	2580*	45	75	2.9	Considerable coal deposits
	Ilyinsky	750	—	—	—	Numerous coal bands 10—15 cm, rarely up to 40—50 cm
P_2	Krasnoyarsk	1600	—	—	—	No coal
	Kuznetsk	1200	—	—	—	Thin coal bands (10—15 cm) in the lower portion
P_1	Balakhonsky	2600	26	78	3	Considerable coal deposits . . . .
C_3	Ostrogsky	600	—	—	—	In the upper portion occasional thin bands of coaly shale . .
		10330	83	166	1.6	

While preserving permanent complexes of flora and fauna in different region of the basin, the isolated series of coal-bearing sediments do not remain constant from the lithological standpoint. Typically the Kuznetsk series is pronounced in

the district of Kemerovo at the western limb of the Kemerovo syncline; at the right-hand bank of the Tom river, opposite to the town of Stalinsk, and in the band of the basin which adjoins Salair. At the eastern marginal part of the basin, in a very good exposure at the right-hand bank of the Tom river, below the issue of the U-Su river and partly along the latter, the Kuznetsk series lithologically shows no such typical aspect. Thick, dark, greenish-grey polymict sandstones, siltstones and arenaceous argillites are predominant there. In a quite different shape this series appears at the eastern limb of the Kemerovo syncline, as may be observed from the exposures of the right-hand bank of the Tom river below the issue of the Gryaznaya river. These deposits were first studied as early as in 1915—1916. Later on they were repeatedly visited by geologists, but literature furnishes very little information concerning them. Meanwhile they fully deserve a detailed study from the standpoint of their lithological composition and still more so from that of their geological structure. It would not be superfluous to note once more (this fact having been repeatedly noted before) that the deposits of the Balakhonsky series developed at this limb, within the interval between the hamlets of Ryabkovsky in the south-east and that of Yermakovsky in the north-west, also deserve to be subjected to a detailed study. It should touch partly upon their lithological composition, but in the main it should be directed towards a study of the qualities and properties of the coals enclosed therein. From their properties these coals differ considerably from those of the Balakhonsky series of other regions of the basin and may prove of great interest for coal-chemical industry.

For the boundary between the deposits of the Balakhonsky and the Kuznetsk series the upper workable coal bed of the former has been arbitrarily adopted. This is a very convenient demarcation, but the real stratigraphic position of this boundary is higher than that; though it cannot be always marked out with sufficient clearness. This fact is of considerable importance when a field geological survey is to be carried out in detail.

In the region under consideration the uppermost bed of the Balakhonsky series is the bed worked by the Poryvaisky mine located at the right-hand bank of the Tom river, 22 km downstream from the village of Krapivino. This coal bed worked by adits is overlain by yellowish-grey sandstones of considerable thickness, lithologically analogous to the sandstones underlying these beds. It may be clearly seen that in their lower half these sandstones are broken into blocks of different size and form by fractures running in different directions. All of these are surrounded along their outer periphery by concentric narrow yellowish-brown bands, 3—5 cm in total width. The intensity of their colouring decreases from the periphery towards the centre. In these sandstones no lamination is observed along the bedding. There are small accumulations of spherosiderite pebbles either in the shape of small lenses, or in separate bands one pebble thick. The interstices between the pebbles are filled in with the same sandstone. On the outside the spherosiderite pebbles are transformed already into limonite. There are also thin (of the thickness of one pebble) conglomerate lenses. Besides, this sandstone contains great quantities of fragments of fossilized trunks of different length and diameter. These show clearly manifested annual rings. They gradually decrease in amount towards the upper half of the sandstones. The sandstones are also traversed by a band of a similar sandstone 1.5 m thick with a clearly perceptible diagonal lamination. Both the composition of this inclusion and the mode of occurrence of the sandstone speak distinctly of its accumulation in the bed portion of a considerable water current, near the littoral region of a reservoir. These sandstone beds are overlain by an 8 m thick layer consisting of alternating lenses of a conglomerate and a coarse-grained sandstone of different sizes. The conglomerate consists chiefly of small quartz and flint pebbles and partly of pebbles of different metamorphic and magmatic rocks.

The pebbly material, among which pebbles up to 10 cm in diameter are occasionally encountered, has not been sorted. This conglomerate is taken here as the boundary between the Balakhonsky and the Kuznetsk series. It is overlain by

a dark-grey argillite of great thickness. While proceeding down the river and studying the deposits of the Kuznetsk series, it may be seen that in their lower portion thick layers of argillites are predominant, while in the upper portion almost exclusively medium- and fine-grained grey sandstones are developed. Siltstones and sandstones in thin bands are scantily represented among the argillites of the lower portion of the series. We do not find here that comparatively close alternation of different rock layers, which is observed e. g. near Stalinsk, at the right-hand bank of the Tom river. That greenish tinge of the rocks, so typical of the Kuznetsk series in other regions, is also absent here. Only in the uppermost horizons of the series do the sandstones acquire a feeble greenish tinge. The cycles, too, are considerably more extensive as compared to those near the towns of Kemerovo and Stalinsk; and are still less clearly manifested than, say, those near the latter town. Now the black shales frequently encountered, e. g. in the rail-road excavations soutwards from the town of Prokopievsk, are present here.

The conglomerate lying at the base of the Kuznetsk series is twice observed here in the exposures along the banks of the river: at about 1.5 km above the village of Poryvaika and near the bend of the Tom river at the mouth of a small hollow, immediately below the village of Poryvaika. Thick green argillites, overlying the conglomerate, form a broad flat syncline. Below the village of Poryvaika the conglomerate forms a distinctly manifested anticlinal fold broken in the arch by an upthrust of small amplitude. The above-mentioned argillites are thrust over the north-eastern limb of the anticline along the underthrust plane steeply dipping towards the north-east. The amplitude of the underthrust is but small. At the north-eastern limb of the anticline we observe NE 10° ∠ 83° and at the south-western—SW 225° ∠ 10°.

The deposits of the Kuznetsk series, flat dipping SW 230—250° ∠ 5—10°, extend along the right-hand bank of the village of Poryvaika, and almost 3 km further on are replaced by the deposits of the Krasnoyarsk series. This replacement takes place gradually. Within this area they form a number of broad slanting synclines with narrow small anticlines between. The north-eastern limbs of these anticlines are steep, the south-western ones are, on the contrary, very flat. Such folds may be observed 800 m above the former village of Spuskovaya, near the latter and in some other places. Along the eroded archs of all these anticlinal folds, except the first, more or less deep hollows are located. The whole of this structure clearly tells of a pressure from the side of the Tomsk-Kolyvyansk massif directed from the north-west to the south-east. As repeatedly shown in literature, it was just this pressure which produced such a complicated folding accompanied by frequent breaks of continuity, westward from the town of Kemerovo within the area between this and the village of Podyakovo.

As shown above, the transition from the Kuznetsk to the Krasnoyarsk series is by degrees. The boundary between these passes along the base surface of the sandstones of this series composing one continuous belt, 1600 m in thickness. While examining this monotonous uniform belt of sandstones stretching over tens of kilometers along the banks of the Tom river, the author was struck by its great thickness and the persistency of the uniform composition. With the above-mentioned geological structure of the deposits of the Kuznetsk series, the sandstones of the Krasnoyarsk series, forming on the whole a great syncline ([2]) and showing a considerable thickness and steep dip at the western limb of the fold near Kemerovo, are at the eastern limb accompanied only by a feebly undulating mode of occurrence. The deposits of both of these series deserve a close study, which is likely to yield very interesting results.

Received
19. XII. 1942.

REFERENCES

[1] В. И. Яворский, С. В. Кулигин и В. Н. Доминиковский. Тр. ВСЕГЕИ, вып. 137 (1941). [2]. П. И. Бутов. Мат. по общ. и прикл. геол., вып. 120 (1926).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

PLANT PHYSIOLOGY

ON THE INTEGRITY OF LATEX VESSEL SYSTEM IN KOK-SAGHYZ AND KRYM-SAGHYZ

By A. A. NICHIPOROVICH

(Communicated by A. N. Bach, Member of the Academy, 10. III. 1943)

Up to the present there is no concurrence of opinion as to the physiological rôle of the latex vessels, of the latex itself and its components in the plant. While it is held by some investigators that latex vessels convey nutrient substances and that the latex is the medium of their translocation and storage, others look upon these vessels as excretory organs and refute the possibility of their conveying any nutrient substance at all.

The latter view is supported usually by the following argument. Namely; it has been established by Bobilioff (1) that the integrity of the latex vessel system in leaves and axial organs of the tropical rubber plant *Hevea* is broken by the presence at the petiole base of abundant accumulations of calcium oxalate crystals which create here a barrier layer separating the leaf's latex vessels from those of the axial organs. From this Bobilioff infers that the rubber is not formed in the leaf, since it could not possibly move from there through the latex tubes to axial organs where its main quantities are known to be concentrated. Even if his conclusion be true, however, one may still point to the fact that in the case of tapping, for instance, there is an abundant outflow of latex from the opened tubes, owing to the influence of turgor pressure exercised on the vessels by the adjoining cells of the parenchyma. It has been established by several different investigators (2-3) that the extent of the outflow zone and, consequently, of the latex movement through the vessels along the axis of the *Hevea* stem is about 1 to 1.5. Frey-Wyssling (2) was able to show that the resistance to the movement of the latex along the stem axis, that is along the main axis of the latex vessels, is nine times as low as in the transverse direction ; i. e. along the anastomoses. This ratio to a great measure determines the bark-cutting technique in tapping the *Hevea* for latex and rubber.

It will be obvious that the question of the integrity of the latex tube system; of its intercommunication upon the transition from one organ to another, of its securing an unobstructed movement in all parts and organs of the plant is a very important one from both practical and theoretical viewpoint. The material reported below throws some light upon it, so far as the rubber plants of this country are concerned.

The method of the experiment was as follows. The roots of plants grown in a field plot under a liberal supply of water were dug up to a depth of 25 cm. On the surface of the torn root tips and cuts some outflow of latex was observed; which coagulated rapidly and plugged the opened vessels. So not all of the available latex came forth, and when the roots were cut again at any place, a renewal of the latex flow was observed. This portion of the latex coagulated again and its flow ceased for the second time. When such cuts were repeated at a distance of 1 to 2 mm apart, beginning from the end of the root, then after 6 or 8 cuts no latex appeared at all, which was evidence that in some zone the turgor pressure of the parenchymal cells had forced out all the latex that could be expressed. Afterwards the cuts were

made in other parts of the root, and the presence or absence of the latex flow was recorded. By this means the extent of the outflow zone could be determined.

The results of these observations are as follows.

Test 1. Five roots were taken; each, 20 to 22 cm long. At the tips of the roots 6 to 7 successive cuts were made by a razor, 1 to 2 mm apart. The last cuts produced no outflow of latex. After that the roots were cut directly under the crown. On these cuts the outflow of latex was either insignificant, or absent at all.

Conclusions. By repeatedly opening the latex vessels at the end of the root it is possible to bring about an outflow of the latex from the root upon a stretch of at least 22—25 cm.

Test 2. Fourty roots were taken as similar in size as possible. Twenty roots were freed from their latex in the above-mentioned way. The roots of the parallel set were fixed by steam immediately after being dug up to be analysed for their rubber content. On a dry matter basis the first 2 samples contained 5.4 and 5.1% of rubber and the second two 6.8 and 6.5%. In this case 22.2% of rubber is extracted from the vessels in the outflowing latex by means of the repeated cuts, or, supposing that the latex flowing out of the latex vessels has an identical composition with the latex remaining in the vessels, one may assume a corresponding quantity for the latex.

Test 3. Two roots branching near the root crown into two equivalent thick roots were taken for the test. The length of each was 21—23 cm. The tip of one of them was cut off by several successive cuts until no latex flow appeared on the last cut. After that the tip of the second branch was cut off. On this cut any outflow of latex was almost entirely absent. And a second cut produced no latex at all. When the two such tips were cut off simultaneously from similar roots, the latex was observed to flow abundantly from both of the branches.

Conclusions. The latex vessels are united into a continuous system extending through all branches of a root. The extraction of the latex from one of the root branches causes its outflow from the other branches.

Test 4. Five roots: from two of them the leaf rosettes were cut off so that all leaves were at once cut through in the base zone. The cut, however, did not touch the growing point and the stem part of the plants. On the cross-sections of the bases the latex appeared in great quantities. The three other plants were freed from their latex by successive cuts made at the end of the roots just as in the Test 1. After the cuts ceased to produce any outflow of latex, these three plants, like the two previous, were stripped of thin leaves. No outflow of latex was observed on the cuts.

Conclusions. The latex vessels of the leaves and roots form a united interconnected system not interrupted; as in the case of *Hevea*, by a separation layer at the base of the leaf petioles. The movement of the latex in the vessels caused by cutting the roots involves not merely the roots, but also the leaves.

Test 5. In the middle of long roots saturated with latex transversed cuts were made half diameter deep into the root. Cuts having the same orientation with respect to the axis of the root were repeated until any outflow of latex ceased from their surface (which presented the form of a semi-circle). In that way «exhausting hollows» of semi-cylindrical form 10—12 mm high were formed in the middle part of the roots. After that the roots were cut up across at a distance of 3, 5, 7 cm from the upper base of the semi-cylinder. At the surface of a complete cut the quantity of latex was abundant only in that semi-circle which stretched over the half untouched by the cut. The semi-circle directly over the cut produced no latex. The nearer the section to the «exhausting hollow», the closer the correspondence between the semi-circle free from the outflow of latex and the upper base of the «exhausting hollow» as regards area, shape and position. Only when the cut was made at a distance of 15 cm from the hollow, did the latex appear on nearly the whole surface of the cut.

Conclusions. Although the latex vessels are richly anastomosed within the limits of each concentrical circle, the movement of the latex in the transverse direction, along the anastomosis, is much more difficult than along the main axes

of the vessels, which fact has been also established by Frey-Wyssling (²) in the case of *Hevea* plants.

Test 6. «Exhausting» cuts similar to those described in test 5 were made at a distance of 2—3 cm from the root crown. After the outflow of latex stopped, the plants were stripped of their leaves, as in test 4. On the petiole cuts situated in that half of the rosette which corresponded to the root half including the «exhausting» cut, the latex appeared in smaller quantity than from petioles located over the untouched part of the root. The difference; however, is not so sharp as in the case of cuts made on roots, and there is no sharp boundary between the «exhausted» and the «not exhausted» half.

Conclusions. The latex vessels of the leaves are united into a single system with the latex vessels of every circle in any part of the root. The intercommunication is materialized in the shortened stem part of kok-saghyz in the immediate vicinity of the growing points. Here the latex vessels are not arranged into regular concentrical circles. On the contrary; they come from the roots to form a very dense network with numerous anastomoses. They are interconnected not only within the same circle; but also in different circles of the same root. As the conducting bundles leave this general network to pass into leaves, there are also latex vessel branches running alongside of them to the leaves. In that way the latex vessels of every leaf are connected with the latex vessels of the root. As the leaves die away, so do also the respective branches of the latex vessels. By this fact, however, the interconnexion between either all or part of the latex vessels and the leaf apparatus is not lost; although the dead leaves with their latex vessel have fallen out of the system, the latex vessels of the root retain their connexion with all of the still living leaves.

Similar results were obtained in the experiments on krym-saghyz. The picture is especially clear when strongly vegetating plants are used in the experiment. These give an abundant outflow of latex (the fall of the first year or the spring of the second).

General Conclusions. The latex vessels in kok-saghyz and krym-saghyz form an integral system in which continuous channels connect the roots with the above-ground organs of the plant. The fact that all portions in our rubber-plants are so distinctly interconnected with one another undoubtedly testifies to the importance of the biological rôle of the system in the life functions of these plants.

K. A. Timiriazev Institute of Plant Physiology.
Academy of Sciences of the USSR.

Received
10. III. 1943.

REFERENCES

[1] W. Bobilioff. Archief v. d. Rubbercultuur Nederl.-Indië, 10,735 (1918); [2] Frey-Wyssling, ibid., 8, 285 (1932). [3] W. Arisz, ibid., 12, 220 (1928).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

ENTOMOLOGY

MELOLONTHA LARVAE AS AFFECTED BY SOIL HUMIDITY

By A. S. KOSMACHEVSKY

(Communicated by A. A. Borissiak, Member of the Academy, 5. III. 1943)

Nearly all investigators who have studied soil insects point out that the humidity of the soil plays an important rôle in the stational distribution of these insects, controlling their vertical localization. At the same time it has also been noted that the influence of moisture is far from being satisfactorily investigated (Kashkarov, 1938; Friderichs, 1932).

As for *Melolontha*, it has been established by the present author that larvae and pupae of this insect thrive at a soil moisture that creates a 100% relative humidity of the air. A soil humidity below this figure results in a loss of water by the larvae, which has upon them a depressive effect. Consequently, the larvae require a soil humidity no less than the maximum hygroscopical one. On the other hand, a soil moisture of 100% to the total moisture capacity creates anaerobic conditions under which the larvae perish.

In order that *Melolontha* eggs enjoy normal development, the soil must contain water which it can easily give off and which can be easily absorbed by the eggs. In the course of their development the eggs absorb twice or thrice their initial weight of soil water. Various investigators (to begin with A. Mayer) have established experimentally that the coefficient of withering of a plant is equal to double hygroscopicity, fluctuating between sesqui- and triple hygroscopicity for various plants and soils. With such a humidity the soil ceases to give off its water to the plant. If the amount of water is below this coefficient, it becomes a «dead stock» being absolutely inaccessible to the plant. This «dead stock» of soil moisture cannot be absorbed by eggs of *Melolontha* either. The eggs require somewhat more soil water than the larvae. They are affected by an excessive soil humidity in the same way as the larvae, while the minimum moisture for eggs must be higher than the double or triple soil hygroscopicity. When studying *Melolontha*, and perhaps some other soil insect, too, it is sufficient to take into account the maximum hygroscopical and the total moisture capacity of the soil, recording water content in the soil in per cent to its total moisture capacity.

The eggs of *Melolontha* are able to develop in humid soil only. If air humidity is at 100% and there is no contact moisture, the eggs are unable to grow. But when put on moistened filtering paper, the eggs develop normally and larvae are hatched. When kept in an atmosphere of humidity below 100%, the eggs perish soon; their membrane bursts and the contents flow out. Owing to water absorption, the eggs swell and their weight increases from two to four times. A freshly deposited egg of *Polyphylla adspersa* Mots. weighs 20—22 mg; before the larva is hatched its weight is 80—90 mg. It is possible to judge of the increase in the weight of the egg, as proceeding at the expense of the water absorbed, from the content of dry matter, as well. Freshly hatched eggs of *Melolontha melolontha* L. contain 30—34% of dry matter, while shortly before hatching it is about 16% to body weight. The swollen eggs are distinguished by their size. A freshly deposited egg of *Polyphylla irrorata* Gebl. has following size: width, 2.5—3 mm, length, 4.5—6 mm, and

after 8—9 days width; 4.5 mm and length; 6 mm. The primary weight is on the average 24 mg, and after 8—9 days it attains up to 72 mg, i. e. increases thrice. During the subsequent days there is almost no increase in weight; and, consequently, the swelling of the eggs proceeds during the first third of their developmental period. Therefore the moisture of the soil must during the developmental period (swelling) of the eggs also be such as to be absorbable by the eggs. After the eggs are swollen, they will be satisfied by a soil humidity that would create a 100% relative humidity of the air. At a higher soil humidity (70% and above of the total moisture capacity) the eggs make no normal development: excessive swelling and insufficient air supply result in their dying-off.

A freshly produced egg of *Amphimallon solstitiale* L. weighs on the average 3 mg, its size being 2.5 × 1.6 mm (index 4.0). Previous to hatching of the larva, the weight of the egg attains 7.4 mg; its length; 3 mm; width; 2.2 (index 6.6).

At first our tests made in order to find out the influence of soil humidity on the development of *Melolontha* larvae were run according to the usual scheme; we took a definite soil sample and obtained the humidity required by adding water. The larvae were put in the soil and supplied with food; after 3—6 days they were weighed, and soil and food changed. By recording the number of larvae that perished in soils with different humidities, we established the optimal moisture. However, under these experimental conditions we obtained discordant data which could hardly be interpreted; and it appeared impossible to explain why the larvae perished in a given soil sample. It was therefore found necessary to reduce the number of larvae in each run; and to closely observe their behaviour. An extra run was added which involved rearing of larvae without soil in closed vials and glasses, with a definite air humidity artificially created in them.

From observations of the behaviour of larvae very interesting data have been secured. First, is has been firmly established that larvae of *Melolontha* can be reared without soil. If they are placed in vessels (glass, test-tube; fixation glass etc.) and given some food (small roots, chopped carrots), they develop quite well. A necessary condition is good air supply to the vessel and a 100% relative air humidity. At a humidity below 100% the larvae do not develop because of water loss by evaporation. The lower the relative humidity and the higher the temperature of the air, the higher is the rate of water loss by the larvae. Larvae of the 3rd instar of *Melolontha hippocastani* F. at 18—20° and at a relative air humidity of 60—80% diminished in weight by 20—35% in the course of 10 days. Larvae of the 3rd instar of *Polyphylla irrorata* Gebl. at a temperature of 17—21° and at a relative air humidity of 50—60% lost during the first fortnight 29—33% of their weight; while during the next fortnight 17—25% more. A loss of more than a half of body weight results in death. If the loss is less than a half weight, when put under favourable conditions again; the larvae are able to feed and augment in weight by some 30—70% in the course of a fortnight. In the subsequent (after 20—40 days) these larvae perish nevertheless. The loss of weight by the larvae proceeds at the expense of water evaporation and of consumption of substances accumulated, since they do not feed during the period concerned.

Secondly; we have found out that dry soil is no favourable medium for *Melolontha*, because the insect is unable to make the furrow in it. In such a soil the larva is always outside, as it were «expulsed» by the powdery soil. The larvae try to dig a furrow, but the sand caves in, and they get higher and higher until they find themselves at the surface. Once upon the surface of dry soil; the larvae cannot dig itself into it again. We observed the same phenomenon in nature, too; the larvae which remained on the surface were destroyed by ants. The larvae cannot normally feed in dry soil.

Clays and black-soils, if very dry (not loosened); become very solid, and the larva cannot dig itself through them. The larvae are poorly mobile in search for food which is rather scarce in such soil. Consequently; the larvae are underfed and become exhausted; which leads ultimately to their death. Solid argillaceous soils are poorly aerated, and the larvae soon consume the oxygen in their stored

furrows; gaseous exchange proceeds very slowly between different soil layers. In the chernozem air supply is sufficient for the larvae.

Thirdly, our observations have shown that the influence of a soil which shows a 100% humidity of the total moisture capacity upon the larvae is no direct, but rather an indirect one. After air supply ceases, the larvae fall at first in a state of stupor; movements and contractions of the spinal vessel (heart) stop; and after some time (5—30 days, according to temperature) the larvae perish. Excessively moist soils (clays and chernozem) become viscous; stick at the larvae; and impede their movement in search for food. Impossibility of feeding and poor air supply are the main factors responsible for the low percentage of larvae of *Melolontha* surviving in soils oversaturated with water. Under experimental conditions; when there was sufficient food and a good air supply, the larvae developed normally in a soil with 100% humidity.

The presence of oxygen in the soil air is a condition necessary for the life of *Melolontha* larvae. The following tests go to illustrate the effect of air deficiency upon them.

The larvae were placed in water; in soil with a 100% humidity; in soil with optimal humidity, but in a closed vessel (a box) with a capacity of 30 cm^3; the store of oxygen was soon exhausted, and the result was invariably the same; after a short period of mobility the larvae fell in a state of stupor which did not cease till they were removed into conditions of good air supply. These runs point to the necessity of the presence of air (oxygen) in the soil in order that the larvae develop normally.

Investigations of breathing showed that larvae of *Polyphylla irrorata* consume during 1 hour 30—100 mm^3 oxygen per 1 g weight (according to temperature and stage of development). A larva of the 3rd instar whose weight is 5—6 g consumes 150—600 mm^3 per hour. A larva must, consequently; continuously move about in the soil in search for optimal air supply. In so far as water and air are antagonistic in the soil; increased humidity calling forth reduced aeration; some students were misled to ascribe to the increase of humidity in the soil a direct influence upon the larvae.

These data bear out the relation between the distribution of larvae and the type of soil. Sandy soils that are better supplied with air, are more densely populated by *Melolontha* larvae and larvae of other insects; provided that they contain adequate food. Contrary to this; clayey soils are not so populated, owing to poor air supply and also because the larvae cannot easily move there.

Kirghizian Institute of Agriculture.

Received
10. VI. 1943.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XL, № 6

PHARMACOLOGY

NEW CARDIACA YIELDING PLANTS FROM THE FAMILY *CRUCIFERAE*

By V. V. REVERDATTO

(Communicated by A. A. Richter, Member of the Academy, 7. IV. 1943)

Plants whose influence upon the heart has been reported and which are known to contain the so-called cardiac glucosides are encountered in different families. Not long ago such plants have been discovered among *Cruciferae*. Under war conditions the search for substitutes of imported vegetable raw material prompted the author to start a detailed investigation of certain representatives of *Cruciferae* with regard to their action upon the organism.

The work carried out in the pharmacological laboratory of the All-Union Institute of Medicinal Plants in 1940 (M. N. Varlakov) has furnished very interesting information concerning a plant of the genus *Erysimum*. On the basis of some data obtained in foreign countries and from his own study of sixteen species of *Erysimum*, three species have been identified by Varlakov (*Erysimum strictum* Gaertn; *E. linifolium* (*Pas*) Gay and *E. cheiranthoides* L.), which he found to surpass in activity the generally known plants containing cardiac glucosides, except the seeds of *Strophantum*. He further expects that new substances can be isolated from these species of *Erysimum*, surpassing in activity the glucosides of *Digitalis* and *Adonis vernalis*, coming close to *Strophantinea* as to the effect produced.

Of the enumerated species of *Erysimum* two are common weeds of Western Siberia, *Erysimum cheiranthoides* L. and *E. Marschallianum* Andrz.; the latter approaching to *E. strictum*.

Varlakov's data have been supported by the results of the investigations of N. V. Vershinin, the well-known pharmacologist. He found *E. cheiranthoides* L. and *E. Marschallianum* Andrz. to be endowed with a very high activity, and the curve of their action upon the heart strikingly to resemble the curve of *Strophantum*. Chemical researches on *E. cheiranthoides* L. have shown this plant to contain a substance giving a positive reaction for cardiac glucosides of stearic structure. The seeds and flowers are especially high in it, in smaller quantities it is found in the leaves, and in still smaller, in the roots. The glucoside obtained was found to be rather unstable: when the plant is preserved, it decomposes rapidly, owing to enzymatic processes.

The efforts of chemists were therefore concentrated on obtaining a preparation pure enough to be introduced into the blood, after the type of *Strophantum* preparations. The chemical properties of the plant and the separation of the glucoside was carried out jointly by the laboratories of the Tomsk University, Tomsk Medical Institute and the All-Union Institute for Experimental Medicine. Experiments on the cultivation of *E. cheiranthoides* L. were run in the Botanical Gardens of the Tomsk University.

According to data by Vershinin, the cultivated plant produces a still stronger effect than the wild one.

During 1942 we collected flowers of *Erysimum altaicum* L. A. M. in the steppe foothills of the Sayan mountain range. The presence of cardiac glucosides in them

was established by chemical reaction, while tests carried out in the laboratory of Prof. Vershinin showed their high physiological activity which is by no means inferior to that of *E. cheiranthoides* L.

During the same time there was collected a great quantity of the flowering herb *Syrenia siliculosa* Andrz. from the Kulundin steppe where it grows very abundantly. On account of the taxonomic position of this genus which stands very near to *Erysimum*, we thought it expedient to test the plant for the presence of cardiac glucosides. And we were not disappointed in our expectations: subjected to chemical investigation at the laboratory of the All-Union Institute for Experimental Medicine (Strochizky analyst), the plant was found to contain a cardiac glucoside, giving a positive reaction to the stearic nucleus. Pharmacological investigations, carried out at the laboratory of Prof. Vershinin, showed the preparation to be an active cardiac, whose effect is similar to that of strophantine. Thus; glucosides of the cardiac group have been found in a new genus, viz. *Syrenia* for which they have never been reported.

The advantage of *Syrenia siliculosa* Andrz. as a pharmacological plant is its most opulent flowering which facilitates the procedure of obtaining a pure preparation, for the seeds always contain vegetable oils.

Now these plants endowed with a strophantine-like activity are being studied in the clinique of Prof. D. D. Yablokov at the Tomsk Medical Institute. Their pharmacological analysis was performed at the Laboratory of Higher Plants of the Tomsk University by the present author and by assistant Prof. Polojy.

The study has been stimulated by the Department of Higher Plants of this University, and carried out by the above-enumerated workers of the Medical Institute and of the Institute for Experimental Medicine; in their work they enjoyed energetic moral support on the part of the latter, and on the part of its vice-director, Prof. B. I. Lavrentiev, in particular.

Tomsk State University.

Received
20. III. 1943.

REFERENCES

[1] М. Н. Варлаков, О фармакологич. активности некоторых видов рода Erysimum. Новое о препарате № 7, 1940. [2] В. Н. Ворошилов, Поиски нового лекарств. сырья, М., 1941.

Prix $ 0.50